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THE PHYSICAL REVIEW

Published monthly Two volumes annually

First series. From July 1, 1893 to January 1, 1913, the Review was conducted by Edward L. Nichols, Ernest Merritt and Frederick Bedell, with the financial support of Cornell University. The first four volumes were issued annually; subsequent volumes, semi-annually; thirty-five volumes, in all.

Second series. On January 1, 1913, the Review was transferred to the American Physical Society as announced on the first page of the new series which was then begun. Since then it has been conducted by a Board of Editors elected by the Society. Semi-annual volumes begin in January and July.

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Annual Subscription, throughout the Postal Union, $7.00 in advance.

Single Copies $.75.

General Index, 1893–1920, $4.00, in advance.

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Advertisements. Rates will be supplied by the Editor on request. Copy for each number must be received at Corning before the 15th of the preceding month; old copy is used until new copy is received. Send electrotypes direct to the printers, George Banta Publishing Co., Menasha, Wisconsin.

Discount of ten per cent is allowed subscription agencies and members of the American Physical Society.

Complaints of failure to receive the Review, in the case of members of the Physical Society, should be addressed to the Treasurer; otherwise, to the Review, Corning, N. Y.

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Entered at the postoffice at Menasha, Wis., as second class matter.
Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917
authorized September 6, 1922

Second Series *April, 1924* *Vol. 23, No. 4*

THE

PHYSICAL REVIEW

THE RECOIL OF ELECTRONS FROM SCATTERED X-RAYS

By Arthur H. Compton and J. C. Hubbard

Abstract

Quantum theory of the recoil of electrons from scattered x-rays.—This is an extension of the quantum theory of scattering suggested by Compton, which assumes that each directed x-ray quantum is scattered by a single electron. Expressions for the *distribution of recoil velocities, of energies and of ranges* are developed for each of two postulates, assuming (1) the scattered radiation consists of directed quanta, and (2) the scattered radiation proceeds as spherical waves. On the first postulate the maximum recoil energy is shown to be $E_m = h\nu_0 \times 2\alpha/(1+2\alpha)$, where $\alpha = h/mc\lambda_0$; the recoil electrons are shown to be concentrated at angles near the direction of the primary beam; and from the distribution of energy, using a relation given by C. T. R. Wilson, the distribution of ranges is found to be such that two-thirds have tracks shorter than half the maximum range. The maximum range increases rapidly with frequency. The values for the maximum ranges in the case of x-rays (.34 to .48 A) are computed to be about one-third of those observed by Wilson for his fish tracts, but the difference may be due to the lack of homogeneity of the rays used. The relative number of recoil electrons to photo-electrons increases with the frequency and is in agreement with observations by Wilson. The second postulate, however, leads to a value for E_m only one-fourth that given above, a value which is inconsistent with that derived from a consideration of radiation pressure and which leads to values for maximum ranges one-fiftieth of those observed by Wilson. Other experimental observations are cited which also lead to the conclusion that the first postulate is much more likely to be true than the second, hence, that each quantum of scattered radiation is probably emitted in a definite direction.

IN recent papers one of the writers has developed a quantum theory of the scattering of x-rays,[1, 2, 3] designed primarily to account for the change in wave-length observed when x-rays are scattered. The postulate upon which this theory is based is that x-rays are scattered quantum by quantum, each from a single electron. The change in momentum of the x-ray quantum on being scattered results in a recoil of the scattering

[1] Compton, Bull. Nat. Res. Council, No. 20, p. 19 (1922)
[2] Compton, Phys. Rev. **21**, 207 and 483, 1923
[3] Cf. also P. Debye, Phys. Zeits. April 15, 1923

electron with a velocity which may be a considerable fraction of the speed of light. When recoiling from the x-ray quanta which they have scattered, these electrons should appear as a type of secondary β-rays. The "recoil electrons" are, however, sharply distinguished from those secondary β-rays known as "photo-electrons," which are ejected with an energy comparable with $h\nu$, in that their energy is less by a factor of the order of γ/λ, where $\gamma = h/mc = 0.0242$ A.[4] In view of their relatively small energy, it is not surprising that at the time this theory was proposed the production of such recoil electrons by x-rays had not been observed. Evidence was, however, presented[5] to show that the secondary β-rays excited by hard γ-rays in the lighter elements are of this type.

Recently a new type of track has been observed almost simultaneously by C. T. R. Wilson[6] and by W. Bothe,[7] in photographs of the passage of x-rays through moist air. These tracks are very short compared with the usual photo-electron tracks, and occur in rapidly increasing numbers as the wave-length diminishes. A tentative suggestion is made by Bothe that these tracks are due to H particles ejected from the water vapor with an energy of about $h\nu$.* This hypothesis leaves unexplained, however, the fact noticed by Wilson that the short-range tracks always proceed in the initial direction of the x-ray beam. Wilson concludes that both the direction and range of the short-range tracks are in agreement with the suggestion that a single electron scatters an x-ray quantum and in so doing receives the momentum of the quantum. Evidence is given below which strongly supports this conclusion. Wilson's discovery of these recoil tracks, following upon the other successes of the theory, makes the evidence very convincing that the postulate of the scattering of whole quanta by individual electrons is sound.

There are, however, two essentially different methods by which an electron may scatter a quantum. In the postulate as first presented it was supposed that an electron receives the radiation quantum from a definite direction and scatters it in a different but equally definite direction. On this view the velocity and direction of recoil of the scattering electron will depend upon the angle at which the quantum is scattered. It may be imagined, on the other hand, that while the energy and momen-

[4] Cf. Compton, l. c.[1] p. 27

[5] Compton, l. c.[1] p. 71

[6] C. T. R. Wilson, Proc. Roy. Soc. A, **104** (Aug. 1, 1923)

[7] W. Bothe, Zeits. f. Phys. **16**, 319 (July 19, 1923)

*Note added March 6: In a second paper, in which Bothe studies these new rays by an ionization method (Zeits. f. Phys. **20**, 237, 1923), he shows that they are electrons instead of H particles. Their range, as he measures it, is slightly less than the theoretical value, Eq. (22), instead of slightly greater, as measured by Wilson.

tum of the primary quantum are received from a definite direction, the energy thus received is scattered in spherical waves in all directions. In this case every scattering electron will recoil in the direction of the primary ray with a momentum equal to the difference between the momentum of the primary ray and the resultant momentum of the spherical scattered ray. While the first form of the postulate is perhaps a more obvious consequence of the general quantum principle, the second form is in better accord with the interpretation of the quantum suggested by C. G. Darwin,[8] and has been used by C. T. R. Wilson in accounting for the short tracks observed in his photographs.[9] By studying the motions of the recoil electrons it should be possible to choose between these two forms of the quantum hypothesis.

Theory of the Recoil Electrons

Their energy. Using the assumption that each quantum of the primary radiation is scattered in a definite direction by a single electron, it has been shown[10] that the relative velocity of the recoil electron is

$$\beta = 2\alpha \sin \tfrac{1}{2}\varphi \frac{\sqrt{1+(2\alpha+\alpha^2)\sin^2 \tfrac{1}{2}\varphi}}{1+2(\alpha+\alpha^2)\sin^2 \tfrac{1}{2}\varphi}, \tag{1}$$

where $\beta = v/c$ and $\alpha = \gamma/\lambda_0$, γ being $h/mc = 0.0242$ A, and λ_0 being the wave-length of the incident x-rays. φ is the angle between the primary and the scattered x-ray quanta. The expression for the kinetic energy corresponding to this velocity, as derived first by Debye,[3] is somewhat simpler, being

$$E = h\nu_0 \frac{2\alpha \sin^2 \tfrac{1}{2}\varphi}{1+2\alpha \sin^2 \tfrac{1}{2}\varphi}. \tag{2}$$

Debye shows further that the angle θ between the primary ray and the path of the recoil electron is given by the expression

$$\tan \theta = -1/(1+\alpha) \tan \tfrac{1}{2}\varphi. \tag{3}$$

Combining these two expressions, it follows that the energy of the recoil electron ejected at an angle θ with the incident ray is

$$E = \frac{2\alpha\, h\nu_0}{1+2\alpha+(1+\alpha)^2 \tan^2\theta} = \frac{2\alpha\, h\nu_0 \cos^2 \theta}{(1+\alpha)^2 - \alpha^2 \cos^2\theta}. \tag{4}$$

The energy of the recoil electron is thus, for small values of α, nearly proportional to $\cos^2\theta$. Its maximum value is at $\theta = 0$, where

$$E_m = h\nu_0 \cdot 2\alpha/(1+2\alpha). \tag{5}$$

[8] C. G. Darwin, Nat. Acad. Sci. Proc. 9, 25 (1923)
[9] Wilson, loc. cit.[6], p. 15
[10] Compton, loc. cit.[2] p. 487

We may calculate the energy of recoil on the second scattering postulate if we notice that the total energy as well as the total momentum of the system (radiation+electron) is the same before and after scattering. The energy equation thus becomes

$$h\nu_0+0=\epsilon_s+mc^2\ (1/\sqrt{1-\beta^2}-1), \tag{6}$$

where ϵ_s is the energy of the scattered radiation; and the momentum equation is

$$h\nu_0/c+0=\mu_s+m\beta c/\sqrt{1-\beta^2}, \tag{7}$$

where μ_s is the momentum of the scattered radiation. To secure a relation between ϵ_s and μ_s we may now make the assumption that the incident radiation is scattered when the electron has a relative velocity $\bar{\beta}=\alpha/(1+\alpha)$, since this is the velocity which the electron must have in order to give the observed change of wave-length according to the Doppler principle.[11] To an observer moving forward with the scattering electron at the velocity $\bar{\beta}c$, the scattered radiation would appear distributed symmetrically in the backward and forward directions, and its total momentum would therefore be zero. The effective velocity of the radiant energy ϵ_s is hence $\bar{\beta}c$, and its resultant momentum is

$$\mu_s=(\epsilon_s/c^2)\bar{\beta}c=(\epsilon_s/c)\ \alpha/(1+\alpha), \tag{8}$$

where, as before, $\alpha=h\nu_0/mc^2$.

By eliminating ϵ_s and μ_s from Eqs. (6), (7), and (8), we find for the relative velocity of the recoil electron, $\beta=\alpha/(1+\alpha)=\bar{\beta}$. Thus the final velocity of recoil of the scattering electron is just that required on the Doppler principle to give rise to the observed change in wave-length. The kinetic energy of a recoil electron with this velocity is

$$E'=h\nu_0\cdot\frac{1}{\alpha}\left\{\frac{1+\alpha}{\sqrt{1+2\alpha}}-1\right\}=h\nu_0\cdot\frac{\frac{1}{2}\alpha}{1+2\alpha}\ (1-\tfrac{1}{4}\ \alpha^2+\ \ldots). \tag{9}$$

Since α is usually small compared with unity, the energy of recoil according to this form of the quantum postulate is almost exactly ¼ of its maximum value (5) according to the first form of the postulate. This result (9) is in accord with the approximate values of the velocity and energy calculated on similar assumptions by one of the writers[4] and by C. T. R. Wilson.[6]

Attention should be called to a difficulty connected with this view of the scattering process. Eqs. (6), (7), and (8) state that the energy and momentum principles are satisfied and that the wave-length change shall be that which is experimentally observed. The equations do not, however, result in kinetic energy of the recoiling electron identical with that

[11] Compton, loc. cit.[2]

which we should calculate from the work done upon the electron by the radiation pressure. The impulse imparted to the electron by the radiation is obviously equal to the difference in momentum of the primary ray and of the scattered ray, i.e.,

$$\int f dt = h\nu_0/c - \mu_s;$$

or substituting the value of μ_s from Eqs. (6), (7), and (8),

$$\int f dt = (h\nu_0/c)\ (1-\alpha+\ \ldots).$$

It is clear, however, that this impulse is imparted while the radiation is being scattered, that is, according to our assumptions, while the electron is moving forward with a velocity $\bar{v} = \alpha c/(1+\alpha)$. The work done on the scattering electron by the radiation pressure is hence

$$W = \bar{v}\int f dt = h\nu_0\ [\alpha/(1+\alpha)]\ (1-\alpha+\ \ldots). \qquad (10)$$

Instead of being equal to the final kinetic energy of the recoiling electron, as given by Eq. (9), this amount of work is about twice as great. It seems

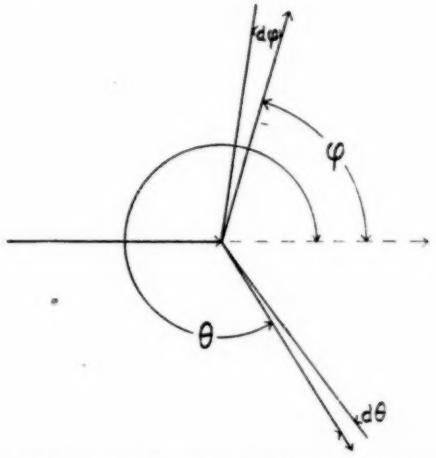

Fig. 1. Electrons which scatter the x-rays in directions between φ and $\varphi+d\varphi$ recoil in directions between θ and $\theta+d\theta$.

impossible to develop a scattering theory on the second form of the quantum postulate (that each scattered quantum proceeds in all directions) without encountering some inconsistency of this character. From the theoretical standpoint we should therefore prefer expression (4) to expression (9) as a statement of the energy of the recoil electrons.

Distribution of the recoil electrons. Let us now determine, on the view that the scattered rays proceed in definite directions, the relative number of electrons which will recoil at different angles. We may suppose, as in Fig. 1, that if the scattered ray proceeds at an angle between φ and $\varphi+d\varphi$ with the incident ray, the recoil electron moves at an angle between

θ and $\theta+d\theta$. Then if $P_\varphi d\varphi$ is the probability that a scattered quantum will lie between φ and $\varphi+d\varphi$, and if $P_\theta d\theta$ is the probability that a recoil electron will be ejected between the angles θ and $\theta+d\theta$, it is clear that

$$P_\theta d\theta = P_\varphi \, d\varphi. \tag{11}$$

In an earlier paper it was shown that[12]

$$P_\varphi \, d\varphi = \tfrac{3}{8} \sin\varphi \, d\varphi \, \frac{(1-\beta^2)\,\{(1+\beta^2)\,(1+\cos^2\varphi)-4\beta\cos\varphi\}}{(1-\beta\cos\varphi)^4},$$

where $\beta = \alpha/(1+\alpha)$. In terms of α this becomes,

$$P_\varphi \, d\varphi = \tfrac{3}{8} \sin\varphi \, d\varphi \, \frac{(1+2\alpha)\,\{1+\cos^2\varphi+2\alpha(1+\alpha)\,(1-\cos\varphi)^2\}}{(1+\alpha-\alpha\cos\varphi)^4}. \tag{12}$$

It follows from Eq. (3) that

$$\tan\tfrac{1}{2}\varphi = -\frac{1}{1+\alpha}\cdot\frac{1}{\tan\theta},$$

whence

$$\left.\begin{aligned} \sin\varphi &= -\frac{2(1+\alpha)\tan\theta}{(1+\alpha)^2\tan^2\theta+1} \\ \cos\varphi &= \frac{(1+\alpha)^2\tan^2\theta-1}{(1+\alpha)^2\tan^2\theta+1} \\ d\varphi &= \frac{2(1+\alpha)\,d\theta}{\cos^2\theta[(1+\alpha)^2\tan^2\theta+1]}. \end{aligned}\right\} \tag{13}$$

Substituting these values in Eq. (12) we obtain for Eq. (11),

$$P_\theta d\theta = -\frac{3(1+\alpha)^2\,(1+2\alpha)\,\{(1+\alpha)^4\tan^4\theta+(1+2\alpha)^2\}}{\{(1+\alpha)^2\tan^2\theta+(1+2\alpha)\}^4}\cdot\frac{\sin\theta}{\cos^3\theta}d\theta.$$

When we write $a=(1+\alpha)^2$ and $b=(1+2\alpha)$, this becomes

$$P_\theta d\theta = -\frac{3ab(a^2\tan^4\theta+b^2)}{(a\tan^2\theta+b)^4}\,\frac{\sin\theta}{\cos^3\theta}d\theta. \tag{14}$$

The probability that a recoil electron will strike unit area placed at a distance R and at an angle θ is

$$P_{R,\theta} = -\frac{P_\theta d\theta}{2\pi R^2\sin\theta d\theta} = \frac{3}{2\pi R^2}\,\frac{ab(a^2\tan^4\theta+b^2)}{(a\tan^2\theta+b)^4\cos^3\theta}. \tag{15}$$

The total number of recoil electrons is, however, equal to the total number of scattered quanta, which has been shown to be,[13]

$$n = (8\pi/3)\; I\, Ne^4/b\; h\nu_0\, m^2c^4,$$

where I is the energy per square cm of the incident ray whose frequency is ν_0, and N is the number of electrons effective in scattering the x-rays.

[12] Compton, loc. cit.[2] p. 492
[13] Compton, loc. cit.[2] p. 493

Combining this with Eq. (15), we find for the number of recoil electrons per unit area,

$$nP_{R,\theta}=4\frac{IaNe^4}{h\nu_0\, R^2m^2c^4}\cdot\frac{a^2\tan^4\theta+b^2}{(a\tan^2\theta+b)^4\cos^3\theta}. \tag{16}$$

Multiplying this by the energy of each recoil electron (Eq. 4), we find for the total energy of the recoil electrons which, if undeviated after scattering the x-ray, should traverse unit area at a distance R and an angle θ with the primary x-ray beam,

$$I_r=\frac{8Iaa\,Ne^4}{R^2m^2c^4}\cdot\frac{a^2\tan^4\theta+b^2}{(a\tan^2\theta+b)^5\cos^3\theta}. \tag{17}$$

The concentration of the effect due to the recoil electrons at angles near the direction of the primary beam becomes apparent when we plot from this Eq. (17) the energy per unit solid angle of the recoil electrons ejected in different directions. This is done in curve A of Fig. 2 for such great

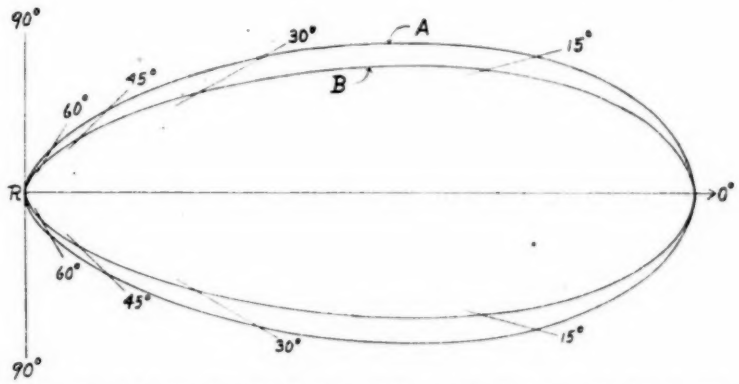

Fig. 2. Spatial intensity distribution of the recoil electrons calculated: A for long waves and B for very short waves ($\lambda=.024$ A) showing a strong concentration near the direction of the incident x-rays.

wave-lengths that a and b are sensibly equal to 1, and in curve B for $\lambda=0.024$ A, corresponding to hard γ-rays. It will be seen that the form of the distribution curve varies but slightly with the wave-length. It is easy to see from this figure, if it is these recoil electrons which constitute the secondary β-rays excited by γ-rays in light elements, how one might conclude with Rutherford[14] and Wilson[6] that the β particles are ejected nearly in the direction of the incident x-rays or γ-rays.

Energy and range of recoil electrons. It remains to determine the probability that a recoil electron will be ejected with a definite energy. If an

[14] E. Rutherford, "Radioactive Substances etc.," p. 276

electron recoiling at an angle θ has an energy E, the probability that the energy of recoil will lie between E and $E+dE$ is

$$P_E dE = P_\theta d\theta. \tag{18}$$

But according to Eq. (4),

$$\tan^2\theta = k/aE - b/a,$$

where $k = 2ah\nu_0$. Thus

$$\frac{\sin\theta}{\cos^3\theta}\, d\theta = \tfrac{1}{2}\, d(\tan^2\theta) = -\frac{k dE}{2aE^2}.$$

Substituting these values in Eq. (14), and noting according to Eq. (5) that the maximum energy of a recoil electron is $E_m = k/b$, Eq. (18) becomes

$$P_E dE = \tfrac{3}{2}\left(1 - 2\,\frac{E}{E_m} + 2\,\frac{E^2}{E_m^2}\right)\frac{dE}{E_m}. \tag{19}$$

This expression is of the same simple form whatever the frequency of the primary rays. In view of the fact, however, that E_m increases with the frequency, the formula can be applied strictly only in case the incident x-rays are homogeneous. Even in this case it is obvious that a correction will usually have to be made for the energy required to remove the recoil electron from the atom.

C. T. R. Wilson has found[6] that the length of his β-ray tracks is proportional to the square of the energy of the β-ray. Writing s for the length of the track and $1/p^2$ as the constant of proportionality, this fact may be expressed as $s = E^2/p^2$, or $E = ps^{\frac{1}{2}}$. When this value of E is substituted in Eq. (19), the probability that the length of the track of a given recoil electron will lie between s and $s+ds$ is found to be,

$$P_s ds = \tfrac{3}{4}\,(1 - 2\,\sqrt{(s/s_m)} + 2(s/s_m)\, ds/\sqrt{s_m s}, \tag{20}$$

whence,

$$P_s s_m = \tfrac{3}{4}\,[\sqrt{(s_m/s)} - 2 + 2\,\sqrt{(s/s_m)}\,], \tag{21}$$

where s_m is the maximum length of the recoil electron tracks.

If we calculate the relative number of tracks of different lengths s/s_m, we find, according to Eq. (21), the values plotted in Fig. 3. It is found that more than two thirds of the tracks are of less than half of the maximum range, and more than one third are of less than one tenth the maximum range. The value of this maximum range may be calculated from the expression for the maximum energy, Eq. (5). Combining this with $s = E^2/p^2$, and writing $\alpha = h\nu_0/mc^2$, we have

$$s_m = \frac{1}{p^2}\cdot\frac{4h^4\,\nu_0^4}{(mc^2 + 2h\nu_0)^2}. \tag{22}$$

It is thus seen that the maximum range increases rapidly with the frequency. These results may be subjected to experimental test.

Another experimental test can be made by comparing the lengths of the photo-electron tracks with those of the recoil electrons. If homogeneous x-rays of frequency ν_0 are used, the highest speed photo-electrons will possess energy $h\nu_0$, whereas the highest speed recoil electrons will possess energy $h\nu_0 \times 2\alpha/(1+2\alpha)$ according to Eq. (4), or approximately $h\nu_0 \times \alpha/2(1+2\alpha)$ according to Eq. (10). The ratio of their energies will thus be either $2\alpha/(1+2\alpha)$ or $\alpha/2(1+2\alpha)$ respectively. The corresponding

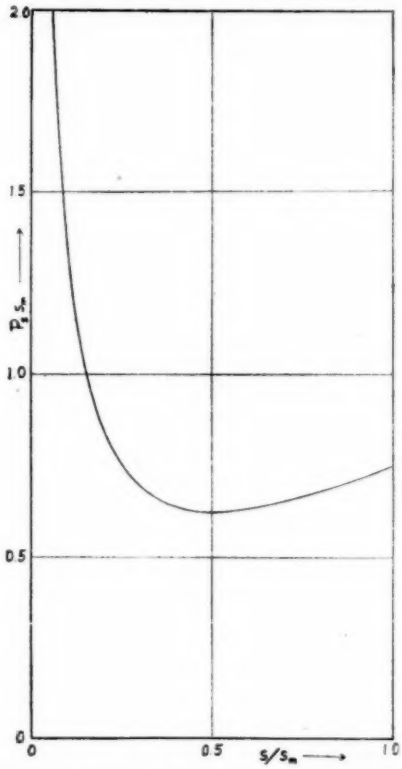

Fig. 3. Most of the recoil electrons have ranges in air less than half the maximum range s_m.

ratios of the lengths of the paths of the photo-electrons and the recoil electrons are

$$R = 4\,\alpha^2/(1+2\alpha)^2 \tag{23}$$

and

$$R' = \alpha^2/4\,(1+2\alpha)^2. \tag{23'}$$

Number of recoil electrons. Each recoil electron represents the loss of one quantum of energy from the primary beam, just as does each photo-electron. It follows that the ratio of the number of recoil electrons to the number of photo-electrons should be equal to the ratio of the x-ray energy

spent in scattering to that spent in exciting photo-electrons. Thus if the total absorption coefficient of the x-rays in the medium is written as $\mu=\tau+\sigma$, where τ represents the energy spent in exciting photo-electrons and σ that dissipated by scattering, the ratio of the number of recoil electrons to the number of photo-electrons is

$$n_r/n_p=\sigma/\tau. \tag{24}$$

This ratio may be estimated approximately from absorption measurements. Since it is found that τ is proportional to λ^3, whereas σ is nearly independent of the wave-length, it follows that for great wave-lengths the photo-electrons will predominate, whereas for small wave-lengths the recoil electrons will be greater in number.

Comparison with Wilson's Cloud Expansion Experiments

Number of tracks. Using the experimental data of Hewlett,[15] we estimate for the wave-length 0.5 A at which Wilson begins to observe the tracks which he attributes to recoil electrons, that $\tau/\rho=0.3$ and $\sigma/\rho=0.2$ per gram, where ρ is the density of the air. Thus there should be about 1.5 times as many photo-electrons as recoil electrons for this wave-length. If his shortest x-rays were about 0.3 A, they should, by similar calculation, have produced about 3.5 times as many recoil electrons as photo-electrons. These numbers are in satisfactory accord with Wilson's observation[6] that the relative number of short range tracks increases rapidly as the wave-length decreases, being greater in number than the long range tracks for wave-lengths shorter than about 0.45 A. This agreement affords a strong confirmation of his conclusion that these short tracks are due to recoil electrons.

Wilson observes in general a predominance of "sphere" tracks over the short range or "fish" tracks. As the frequency increases the sphere tracks increase rapidly in number,[6] and are accompanied by the development of fish tracks. These observations coincide in detail with what would be expected in view of Eqs. (21) and (22). The great predominance of points or sphere tracks in Wilson's photographs may be attributed to the relatively great probability of tracks of vanishingly small range, and on the other hand, the rapid development with increasing frequency of these points into tracks of measurable length is in agreement with the expression for the maximum range of a single particle as a function of the frequency, given in Eq. (22). The close general agreement between the experiments and the theory leads to the conclusion that the sphere tracks as well as those of definite range must be considered together in any study of x-ray scattering. In order that quantitative comparisons be-

[15] C. W. Hewlett, Phys. Rev. **17**, 284 (1921)

tween experiment and theory may be made, it is desirable that data be secured on the tracks produced by homogeneous x-rays.

Range of tracks. Eqs. (23) show that the recoil electrons with the longest paths should go 16 times as far on the directed quantum hypothesis as on the spherical radiation view. Wilson observes that "When the x-rays are hard enough to eject β-particles of 1.5 cm range, fish tracks of ranges up to about 0.4 mm appear; their range increases as the frequency of the incident radiation is increased, but rarely exceeds 1.5 mm, even when the long tracks have a range exceeding 3 cm."[6] The wave-length required to produce a photo-electron track of 1.5 cm length, according to Wilson's data, is about 0.48 A, whence $\alpha = .0242/.48 = .050$. According to Eq. (23) the longest recoil tracks should thus be $1.5 \times 4\alpha^2/(1+2\alpha)^2 = 0.12$ mm. While this is considerably shorter than the observed tracks of 0.4 mm, it is at least of the correct order of magnitude. Eq. (23), however, would predict a track of only 0.008 mm length, which is very much too short.

Similarly, corresponding to the long tracks of 3 cm range, for which the wave-length is 0.34 A, Eq. (23) predicts recoil tracks of 0.5 mm length and Eq. (23′) of 0.03 mm. The difference between the theoretical range of 0.5 mm and the observed range of 1.5 mm is perhaps no greater than might result from the fact that heterogeneous x-rays were used by Wilson in these experiments. For the number of photo-electrons excited in air increases rapidly with increasing wave-length whereas the prominence of the recoil electrons decreases with increasing wave-length. Thus the effective wave-length for the photo-electrons must have been greater than that for the recoil electrons. This consideration certainly accounts for a part of the difference between the theoretical and the experimental values. In order to obtain a more exact test of Eq. (23) it will be necessary to excite the recoil electrons by more nearly homogeneous x-rays.

The present experiments of Wilson suffice to show, however, that Eq. (23′), which leads to a range differing from the experimental value by a factor of about 50, is not correct. This indicates that we must abandon the assumption upon which the equation is based, that the scattered radiation is emitted in spherical waves. Both from the standpoint of the experimental evidence and from the internal consistency of the theory *we therefore seem forced to the conclusion that each quantum of scattered x-rays is emitted in a definite direction.* It would appear but a short step to the conclusion that all radiation occurs as definitely directed quanta rather than as spherical waves.

THE UNIVERSITY OF CHICAGO (A. H. C.)
NEW YORK UNIVERSITY (J. C. H.)
October 25, 1923.

IONIZATION OF GASES AS A FUNCTION OF THE ENERGY OF ELECTRON IMPACTS

By A. Ll. Hughes and Elias Klein

Abstract

Ionization of various gases by electrons of energy up to 300 volts.—Electrons were accelerated from a tungsten wire to a plane perforated electrode G, through which a small fraction passed into a space where they were all stopped by a retarding field between the perforated electrode and a plane parallel plate P connected to an electrometer, which collected all the positive ions formed on collision between the electrons and the gas molecules. *The fraction of the collisions resulting in ionization* as a function of the energy of impact is shown to be $f(V') = (1/2apD)[d(V_0P/E)/dV_0]$, where P/E is the ratio of positive ions produced to the number of electrons passing through the perforated electrode G, V_0 is the retarding potential between P and G and is somewhat greater than V' the maximum energy of impact, p is the pressure, D the distance apart of P and G, and a is the chance of collision per cm for 1 mm pressure which is assumed to have the Kinetic Theory value. For *helium*, *neon*, *argon*, *hydrogen*, *nitrogen*, and *methane*, $f(V')$ was found to increase very rapidly to a maximum value, after which there was a less rapid, though marked, decrease. The maxima occur at 147, 157, 80, 74, 101, and 80 volts for the gases in the order named, the maximum values being respectively .11, .14, .35, .21, .32, and .28. Even for the most favorable velocities, then, less than half of the collisions result in ionization.

Radiation potentials of argon and carbon. A break in the argon curve suggests *L radiation for argon* at 250 volts impact energy, while a break in methane curve indicates a possible *K radiation for carbon* at 248 volts.

THE purpose of this investigation is to determine experimentally the percentage of molecules of a gas ionized by electron impacts as a function of the energy of impact. It is well known on the one hand that high speed electrons (β rays) pass through molecules much oftener without ionizing them than electrons having moderate speeds and are therefore to be regarded as inefficient ionizing agents, while on the other hand, electrons having energies below the ionizing potential do not ionize normal molecules at all. In between these limits, there must be a value of the impact energy at which the electron has its maximum efficiency as an ionizing agent.

Much work has been done on the measurement of the critical threshold energy which the electron must have in order just to produce ionization, the ionizing potential of course being a measure of this energy. Little is known, however, as to the percentage of collisions between electrons and molecules, which result in the formation of ions, at any value of the energy of impact.

This investigation is part of a general attack planned by one of the authors on the measurement of various effects as a function of the energy of impact of the electron on the molecule. Thus the distribution of the intensities in the spectrum has been studied as a function of the energy of impact for hydrogen[1] and helium,[2] and the dissociation of hydrogen[3] has been investigated as a function of the energy of electronic impacts.

It is hoped ultimately to get for a number of gases, as a function of the energy of impact of the electrons on the molecules, the percentage of collisions resulting in ionization, the percentage resulting in dissociation (for polyatomic gases), the distribution of intensities in the spectra and the intensity of the radiation which can be measured photo-electrically. The latter is, of course, merely a quantitative study of the effect started at the radiating potential and carried to much higher energies of impact. It is a makeshift for measuring the distribution of intensities in the

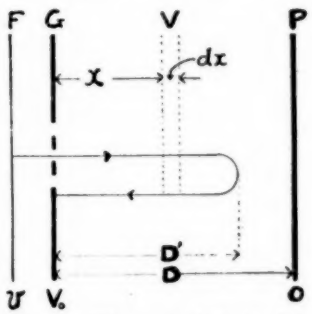

Fig. 1. Diagram of electrodes.

spectrum in the extreme ultra-violet region as we have at present no easy way of measuring intensities of spectrum lines in this region. In all these experiments, the underlying idea is to study the effect of impact between an electron and a *normal* molecule, so that to avoid cumulative effects we have to work with as feeble electron currents and with as low pressures as is practicable.

The arrangement employed for studying the ionization at different energies of impact was much the same as that used in the original Lenard method of studying ionizing potentials. Electrons are accelerated from a thermionic source F through very small holes in the electrode G (Fig. 1).

[1] Hughes and Lowe, Phys. Rev. **21**, 292, 1923

[2] Hughes and Lowe, Proc. Roy. Soc. **104**, 480, 1923

[3] Hughes, Phil. Mag. **41**, 778, 1921. The results of this research are not strictly comparable with the others, since the results were given as a function of the terminal maximum electron energies, that is, the electrons used had a range of energies from zero up to a maximum. In the present investigation and in the spectrum researches the results are given as functions of the actual electron energies on impact.

Beyond G they are subjected to a retarding field between the parallel plane electrodes P and G. A small positive potential v is applied to F to prevent the electrons reaching P, which is at zero potential. The gas pressure is generally sufficiently low to ensure that only one electron in about ten collides with a molecule in the distance GP (9 mm) so that the chances of an electron making two collisions are less than one in a hundred.

Reducing the gas pressure, however, does not get rid of the secondary electrons produced on the right hand surface of G when the primary electrons strike it on their return journey. However, although the error due to not taking these secondary electrons into account is difficult to estimate, it is believed to be quite small.

Let E = number of electrons passing into the space GP per second; p = gas pressure.

The number of collisions per second between electrons and molecules in dx, is

$$dN = \alpha p E\, dx,$$

where α is the constant giving the number of collisions made by one electron in 1 cm path at 1 mm pressure.

The number of positive ions produced in dx is

$$dP = 2dN\, f(V')$$

where V' is the energy, expressed in volts, of the electrons as they pass through dx, and $f(V')$ is the unknown function giving the fraction of collisions resulting in ions at this energy of impact, which is sought in this investigation. The 2 takes care of the ions formed on the return journey through dx.

Hence

$$dP = 2\alpha p E dx\, f(V').$$

The relation between V', which measures the energy of the electrons at the equipotential surface x, and the potential V of that surface is

$$V' = V - v.$$

v may include, besides the potential of F, the correction due to initial velocities of the electrons from F, the contact potential difference, etc.

$$\frac{D-D'}{D} = \frac{v}{V_0}; \quad \frac{D-x}{D} = \frac{V}{V_0}; \quad dx = -\frac{D}{V_0}\, dV$$

$$P = -2\alpha\, p\, E(D/V_0) \int_{v_0}^{v} f(V-v)\, d\, V$$

$$P\, V_0 = -2\alpha\, p\, ED\, [F(v-v) - F(V_0-v)]$$

$$d(PV_0)/dV_0 = 2\alpha\, p\, ED\, f(V_0-v)$$

Hence the required function

$$f(V_0') = f(V_0 - v) = \frac{1}{2a\ p\ D} \cdot \frac{d(V_0\ P/E)}{dV_0}. \tag{1}$$

To get it experimentally, we must measure the positive ion current P per unit electron current, passing into the space GP, as a function of the potential V_0 of the electrode G, then form the product $V_0\ P/E$, plot it against V_0 and differentiate graphically, or else plot successive differences

$$(V'_0P'/E' - V''_0P''/E'')/(V'_0 - V''_0).$$

Apparatus and Method of Experiment

The final form of apparatus is shown in Fig. 2. It consisted of a pyrex tube 4 cm in diameter. The electrode G was a flat sheet of nickel hard soldered to a long cylinder of nickel so that the filament F was shielded from glass surfaces which might be at variable and indefinite potentials. The nickel cylinder fitted tightly into a glass tube of 3 cm diameter which

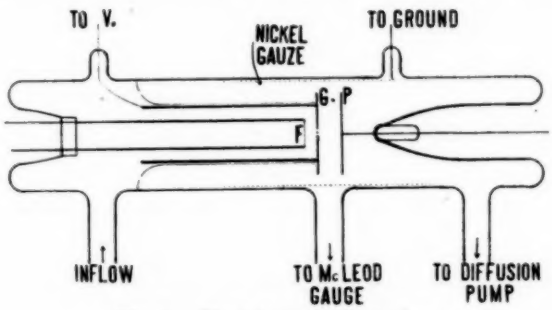

Fig. 2. Final form of apparatus.

was fused to the main tube at three points around the circumference. This permitted the gas to flow freely through the apparatus. In a region, 8 mm × 2 mm, in the center of G were drilled about 40 holes, .2 mm in diameter, through which the electrons passed into the space GP. A grounded nickel gauze inside the pyrex tube about G and P served to define the potential in the vicinity. In the helium experiments, helium was purified by passing through a charcoal tube in liquid air into a reservoir holding about 100 cc. From this reservoir it was passed into the apparatus through a fine capillary capable of transferring .2 cc per hour with a driving pressure of one atmosphere in the reservoir and a vacuum in the apparatus. Between the capillary and the experimental tube (Fig. 2) the helium was again purified, now at low pressure, by passing it through another charcoal tube in liquid air. When other gases were used, the charcoal in this liquid air tube was omitted. The other tubes

leading to the pump and the gauge contained liquid air traps. All traps were left submerged in liquid air for the whole period during which any one gas was under investigation. The diffusion pump was in action continuously and a very steady pressure of gas was maintained in the apparatus.

Electron current. The total electron current from F to G was measured by means of a Leeds and Northrup galvanometer provided with a variety of shunts. To get the fraction of electrons passing through into the space GP, we arranged to measure simultaneously the electron currents to G and to P when the potentials of F, G, and P, were 0, V_0, and X volts respectively. Keeping V_0 constant and varying X, the number of electrons going to P increased rapidly as the value of X passed through V_0, and as X approached $2V_0$ the number of electrons became practically constant, showing a slight uniform linear increase with voltage beyond $2V_0$. The reason for this of course is that the electrons impinging on P excite secondary electrons at P having energies ranging all the way from zero to those of the primary electrons. These will only be held back completely when $X=2V_0$. The slight linear increase beyond $2V_0$ is due to the holes in G not being infinitely small, so that increasing the field considerably in GP pulls some more electrons through the holes. Since in the positive ion experiments the potential of P is zero, the obvious thing to do to get the actual fraction of the electrons passing through when $X=0$ is to extrapolate the almost flat linear portion of the curve back to the zero axis. This procedure was carried out for six different values of V_0 and a curve was drawn showing the number of electrons E passing through the holes in G as a function of the number going to G itself for different values of V_0, when $X=0$.

Positive ion current. The current to P was measured by means of a Dolezalek electrometer, shunted by an India ink resistance on cardboard sealed up in a glass tube. The values of the resistances were measured at frequent intervals to correct for slight progressive changes.

The plotted curves are the mean curves of at least four runs (generally eight) up and down the range of voltages. In certain cases, e.g., around certain voltages at which soft x-rays might be expected, as many as twenty runs were averaged to give the curve so as to show up any slight discontinuity which might be present.

The determination of the absolute value of $f(V')$ depends upon the values of D, α, p, and the gradient of the $V_0(P/E)$ curve. $D=.90$ ($\pm .03$) cm. α, the number of collisions made by an electron in moving 1 cm through the gas at 1 mm pressure, is the most uncertain of the constants used. According to the Kinetic Theory of Gases, an infinitely small particle,

such as an electron, would make 7.95 collision per cm in helium at 1 mm pressure. A number of investigations by Lenard, Townsend, Compton, Meyer, and Ramsauer on the motion of electrons in gases, have led to numerical values for α. Unfortunately, these differ so much among themselves, and there seems to be no obvious reason why one should be taken in preference to the others, that we have decided to adopt the value given by the Kinetic Theory of Gases. Should future research on the motion of electrons in gases lead to a more acceptable value for α, the results in this investigation can easily be corrected by a suitable factor. At the pressure used for helium, .0048 mm, the collision frequency per cm path is $.0048 \times 7.95 = .0382$, which means that the chances of any electron making a *second* collision, may be neglected. The relative values of the collision frequency in the various gases used, are given in the following table together with the actual collision frequencies at 1 mm pressure.

Gas	:	He	H_2	N_2	A	Ne	CH_4
Relative collision frequency	:	1.00	1.54	2.96	2.77	1.6	3.64
Actual ($p = 1$ mm)	:	7.95	12.24	23.53	22.02	12.80	28.94

The actual energy of the electrons obtained with any applied voltage is not given accurately by that voltage minus v, the voltage applied to the filament. Corrections have to be made for initial velocities of emmission, contact potential difference, voltage fall along the filament, etc. The corrections were made by noting the values of the applied potential V_0 at which the discontinuities corresponding to the ionizing potential appeared. At these points, the actual values of the electron energies are given by the ionizing potential, and the necessary correction to get the electron energies at all points is therefore given by the difference between V_0 and the ionizing potential. In the curves shown, the electron energies, so obtained, are indicated as well as the values of V_0. The values of the ionizing potentials assumed are as follows, in volts: He, 24.5; Ne, 22.2; A, 16.0; N_2, 17.0; H_2, 16.2; CH_4, 13.9.

In each diagram will be found three curves. First, we have the experimental curve P/E, the absolute value being shown on the right hand ordinate. The second curve, showing $V_0(P/E)$, is obtained by multiplying each experimental value P/E by the corresponding V_0. The third curve $f(V')$ is obtained by graphical differentiation of the second curve, and its absolute value calculated from Eq. (1). The values of $f(V')$ are shown on the left hand ordinate of the curves.

Two diagrams are given for each gas, one showing the curves over the whole range, and one showing the curves over the earlier part of the range.

Helium and Neon

The helium was purified as described earlier in the paper. The neon was obtained from the Linde company, and was stated to be over 99 per

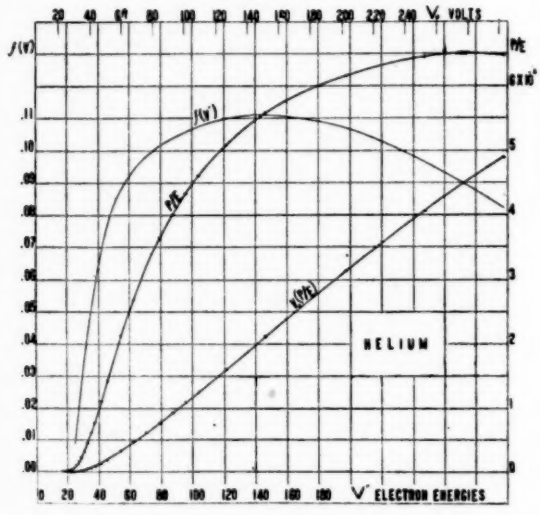

Fig. 3a

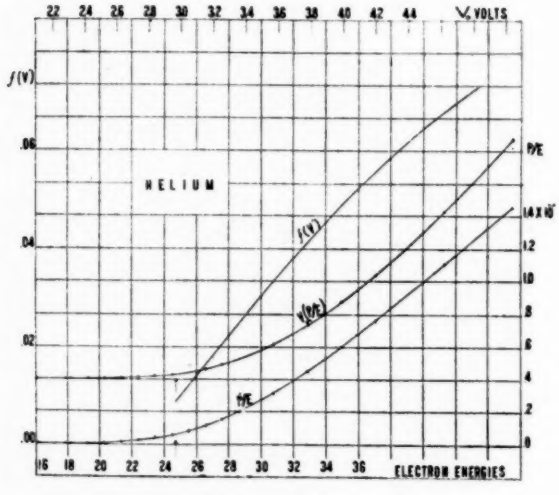

Fig. 3b

cent neon. According to the company, there was not even a spectroscopic trace of helium in the neon. The curves for these two gases are given in Figs. 3a, 3b, 4a, 4b. The $f(V')$ curves are very similar in character, although the gases were certainly not alike as the viscosities of the

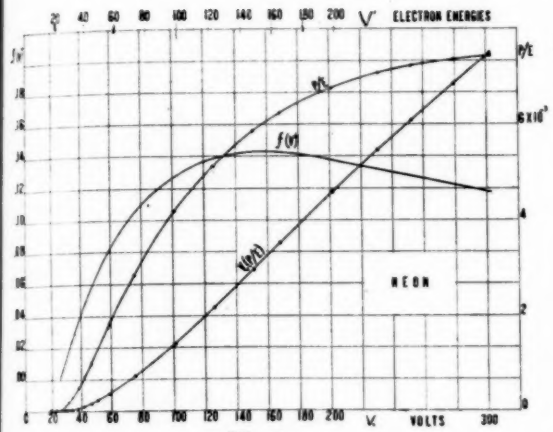

Fig. 4a

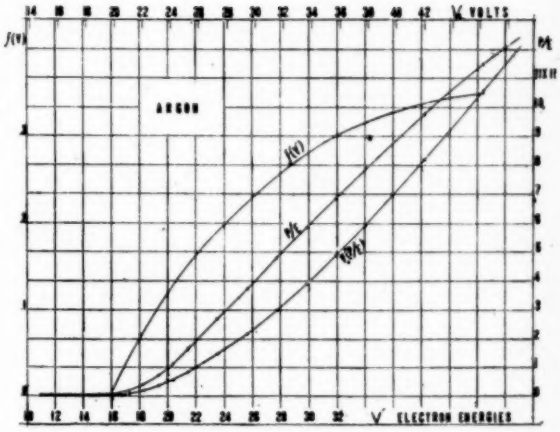

Fig. 5b

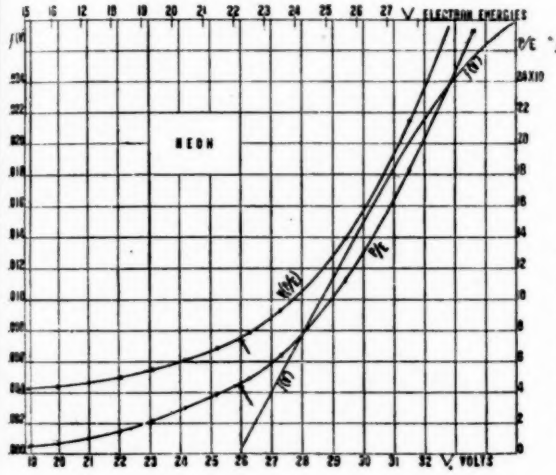

Fig. 4b

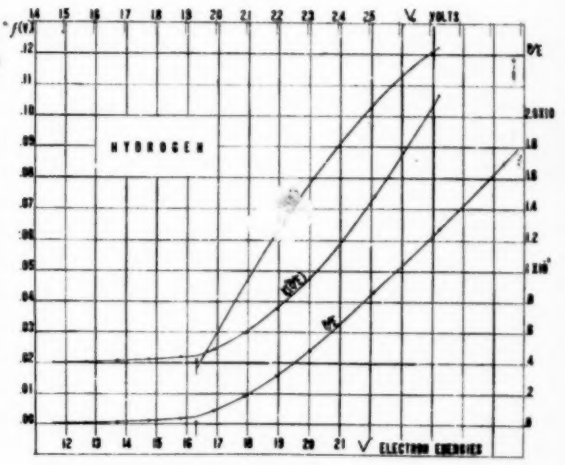

Fig. 6a

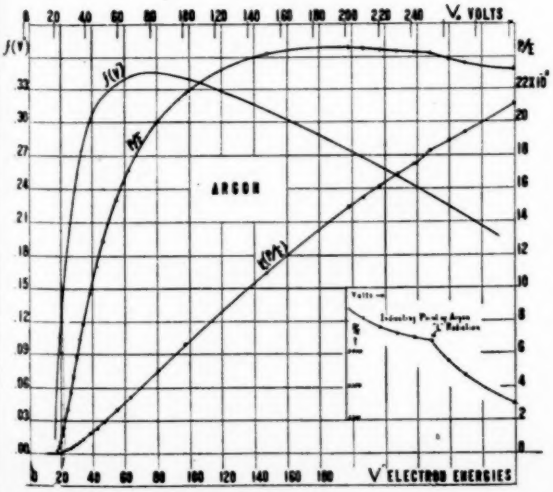

Fig. 5a

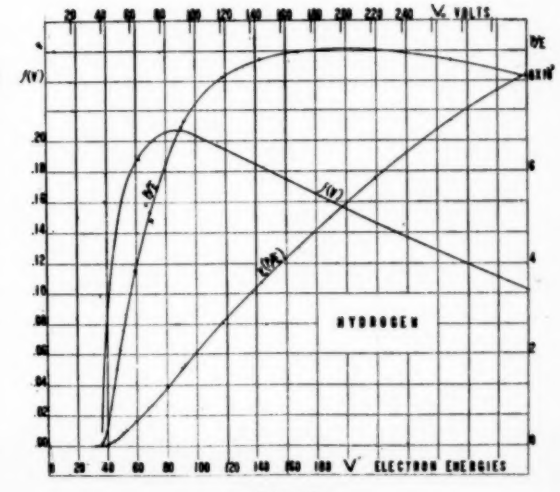

Fig. 6b

two gases, as indicated by the rate of flow through the apparatus, were widely different.

Argon

Argon of purity 99.8 per cent was used. The results are shown in Figs. 5a and 5b. The maximum value of $f(V')$ for argon is higher than that

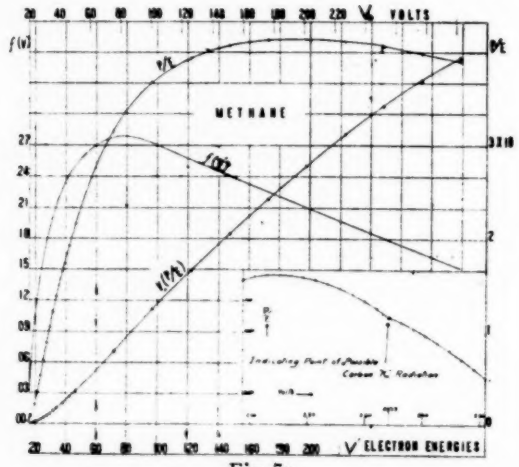

Fig. 7a

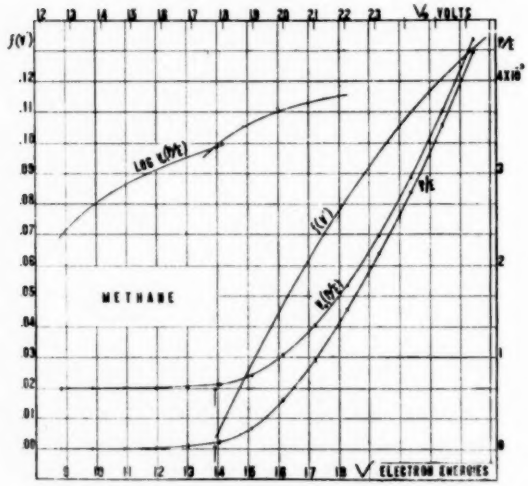

Fig. 7b

for any other gas investigated, and it occurs much earlier than with helium or neon. As a subsidiary experiment, a search was made for a possible discontinuity in argon, corresponding to the L radiation. In the lower right hand corner of Fig. 5a, will be found a large scale P/E diagram, showing a break at 250 volts.

Hydrogen, Nitrogen and Methane

The $f(V')$ curves for these three gases are similar to one another. To get the ionizing potential break in methane and in nitrogen, it was found that plotting log (V_0P/E) indicated the critical point more definitely

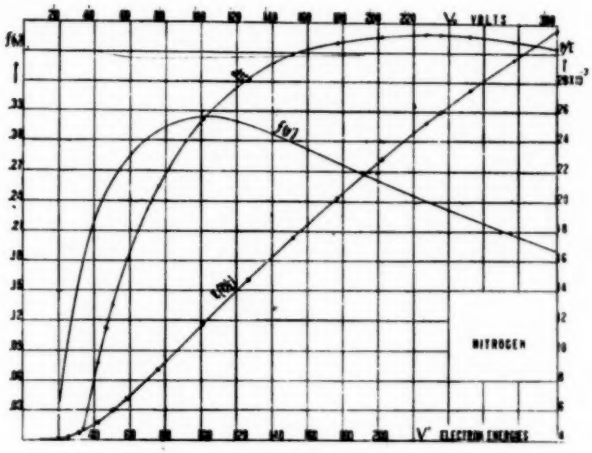

Fig. 8a

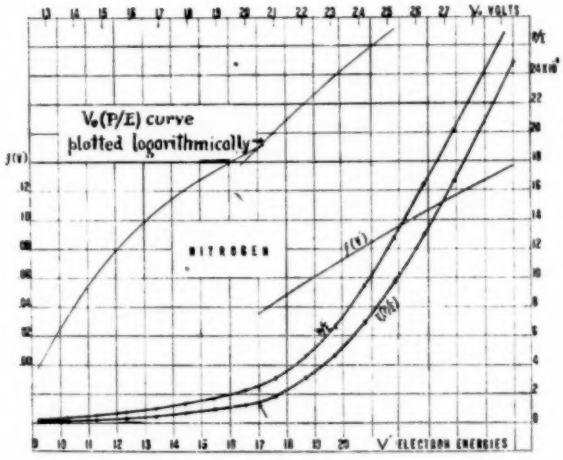

Fig. 8b

than either the P/E or the V_0 (P/E) curve. A very carefully taken set of twenty runs between 200 and 300 volts in methane showed in the mean curve, a small but definite break at about 244 volts. This may be the K critical point for carbon.

Discussion

In order to compare the $f(V')$ curves for the different gases, they are all plotted together, Fig. 9, as functions of the electron energies expressed in volts. The following observations may be made.

The maximum value of $f(V')$ for the polyatomic gases increases regularly with the molecular weight (2, 16, 28). The value of the electron energy at which $f(V')$ is a maximum, also increases regularly with increase of molecular weight. For the monatomic gases the maximum value of $f(V')$ also increases with increasing atomic weight (4, 20, 40),

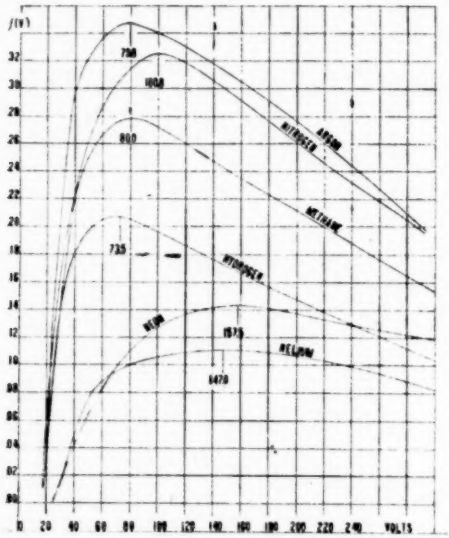

Fig. 9

but no generalization as to the value of the electron energy at which $f(V')$ is a maximum can be made. The tendency, however, is for it to run in the opposite direction to that noted in the polyatomic gases.

The number of electrons per molecule is perhaps of more significance than the molecular weight. These run in the order 2, 10, and 14 for H_2, CH_4 and N_2; and in the order 2, 10, and 18, for He, Ne, and A. The same qualitative statements as made in connection with molecular weight will apply when we consider the number of electrons per molecule.

In argon, under the most favorable circumstances, one collision out of three results in ionization, while in helium the maximum proportion is one out of ten.

With the method employed, it is impossible to distinguish between positive ions and a photo-electron effect due to radiation. Except just above the ionizing potential, it is believed that the radiation effect may be considered negligible in comparison with the positive ion effect. Be-

low the ionizing potential, the small apparent ionization is really due to a photo-electric effect at P excited by radiation produced between the ionizing and radiating potentials.

It is perhaps worth while stating, what has already been said in different terms, that the absolute value of these fractions is in doubt to the same extent as is the assumed value of the frequency of collisions between electrons and atoms.

Ramsauer[4] has recently published an account of his measurements on the collision frequency between electrons and atoms in argon and other gases. He finds, for example, that the collision frequency in argon is much *less* than the Kinetic Theory value for electron energies of the order of 1 volt, but increases rapidly to a maximum at about 12 volts where the experimental value is 4.4 times *greater* than the Kinetic Theory value. In the region overlapping that studied in this paper, the ratio of the experimental value to the Kinetic Theory value falls off to nearly unity at 100 volts. The values of the ratio at the voltages 16, 25, 36, 49, 64, 81, 100 are 3.8, 2.6, 1.5, 1.2, 1.1 and 1.06 respectively. This means that if we were to take Ramsauer's values in preference to the Kinetic Theory values, we should have to diminish the ordinates in these ratios. The effect would be more marked, the lower the voltage. The position of the maximum would hardly be affected, the shift being a few volts towards higher voltages. The values of $f(V')$ at the maximum would be diminished by about 10 per cent.

The curves have a number of characteristics in common. They all show a well marked maximum, preceded by a very rapid rise from the ionizing potential and followed by a distinct, though less rapid, fall. On the high voltage side, they all show (with the doubtful exception of Ne), a tendency to meet the abscissa axis at points between 600 and 700 volts. It would be interesting to carry out experiments in this region to see if, as suggested by the extrapolation, the ionizing power of electrons of this speed is almost zero.

The derivation of $f(V')$ shows that it varies inversely as the value of α, the frequency of collision between electrons and molecules per cm path at 1 mm pressure. Hence $\alpha f(V')$ is independent of the value of α, and *measures the number of positive ions produced per cm path at 1 mm pressure* when the electron is moving with energy V'. As there is considerable doubt as to the proper value to assume for the collision frequency, it is desirable to express the results in a form not dependent on α, and this is secured in Table I which gives the values of $\alpha f(V')$ whereas the curves give $f(V')$. Should these results be used for testing theories, the values given in the table are more accurate than those which could be measured

[4] Ramsauer, Ann. der Phys. **72**, 346, 1923

from the curves. The values are given to three significant figures. This does not mean that the absolute values are correct to this extent, for there was an uncertainty of 3 to 4 per cent in determining d the distance between G and P; but the relative values at different electron energies are considerably more accurate. The numbers in brackets beside the symbols for the gases are the numbers of electrons per molecule.

TABLE I

Ions formed per cm path at 1 mm pressure, a $f(V')$

Energy	He(2)	Ne(10)	A(18)	H_2(2)	N_2(14)	CH_4(10)
300 volts	.648	1.502	4.14	1.264	4.460	4.36
280	.699	1.557	4.54	1.362	4.775	4.72
260	.744	1.608	4.83	1.463	5.100	5.05
240	.782	1.666	5.31	1.568	5.420	5.41
220	.815	1.710	5.68	1.678	5.650	5.74
200	.844	1.754	6.03	1.785	6.080	6.20
180	.867	1.800	6.36	1.902	6.425	6.43
160	.880	1.828	6.67	2.018	6.780	6.78
140	.881	1.820	6.95	2.137	7.125	7.14
120	.870	1.768	7.21	2.260	7.450	7.47
100	.846	1.651	7.45	2.376	7.640	7.82
80	.804	1.450	7.65	2.487	7.470	8.06
60	.730	1.130	7.48	2.518	6.880	7.80
40	.500	.630	6.74	2.280	5.580	6.79
35	.380	.480	6.36	2.153	4.96	6.28
30	.229	.320	5.56	1.947	4.09	5.55
29	.192	.287	5.35	1.882	3.89	5.37
28	.155	.255	5.13	1.825	3.68	5.20
27	.120	.220	4.88	1.755	3.47	5.00
26	.082	.180	4.61	1.670	3.24	4.80
25	(24.5)*	.140	4.31	1.600	3.02	4.55
24		.095	4.00	1.500	2.80	4.30
23		.044	3.67	1.383	2.54	4.02
22		(22.2)*	3.30	1.260	2.28	3.72
21			2.90	1.130	2.00	3.40
20			2.45	.980	1.72	3.05
19			1.90	.800	1.42	2.67
18			1.29	.595	.80	2.26
17			.45	.350	(17.0)*	1.80
16			(16.0)*	(16.2)*		1.28
15						.75
14						.10
						(13.9)*

*Ionization potential in volts.

It is clear that whether ionization occurs or does not occur on collision is not determined merely by whether the energy of the electron exceeds or does not exceed the ionizing potential, as has sometimes been tacitly assumed. When the electron has energies just above the ionizing potential, only the most favorable conditions at impact, e.g., those of orientation, yield ions. As the impact energy is increased, conditions of im-

pact for ionization become less exacting, with a consequent increase in the number of collisions resulting in ions, until the maximum is reached. Beyond this point, even though the energy conditions are more than satisfied, the *time* during which the electron acts on the atomic system becomes less and less, with the result that fewer and fewer collisions result in ionization. Thus there are two factors concerned, viz., energy and speed. The ionizing potential measures the minimum energy necessary to produce ionization, even under the most favorable conditions, while the position of the maximum in these experiments gives a measure of the time of action between the electron and the molecule, resulting in the best yield of ions.

It seems impossible to handle the problem quantitatively at the present time. We may attempt a comparison of the time taken by the electron in the hydrogen *atom* (chosen for its simplicity) to move in its orbit from one end of the diameter to the other, with that of an electron shooting through the system. When the electron belonging to the atom happens to be travelling in the same direction as the electron shooting into the system, one would expect the disrupting effect of the impacting electron to be appreciable as long as they both traverse the atom in about the same time, but to decrease when the speed of the impacting electron takes it across the atom much faster than the electron belonging to the atom. According to Bohr's theory, the electron in the hydrogen atom moves from one end of a diameter to the other in its path around the orbit in $.7\times10^{-16}$ second. An electron having an energy 75 volts (giving maximum $f(V')$ for hydrogen), would traverse the diameter in $.2\times10^{-16}$ second, which is considerably shorter, though of the same order. It is of course admitted that these considerations are not strictly applicable to our work, as we are dealing with hydrogen molecules, not atoms. For want of satisfactory data on the molecule, we are forced to this makeshift.

Provided we consider the monatomic and the polyatomic gases separately, and make no intercomparisons, our results suggest that the maximum value of $f(V')$ (and indeed practically the whole curve) is higher, the more electrons there are in the molecule.

We wish to express our best thanks to Dr. E. F. Nichols for the opportunity of carrying out this investigation at the Nela Research Laboratories during the summer of 1923, and for giving us every facility and assistance in our work.

NELA RESEARCH LABORATORIES,
NATIONAL LAMP WORKS,
CLEVELAND, OHIO,
August, 1923.[5]

[5] Received November 9, 1923—Ed.

A METHOD FOR THE ESTIMATION OF THE AVERAGE LIFE OF EXCITED MERCURY ATOMS

By Louis A. Turner

Abstract

Average life of excited mercury atoms.—(1) *In mixtures with hydrogen, computed from rate of dissociation of hydrogen,* found by Franck and Cario. A theory is developed which gives the relation between the rate of dissociation of H_2 molecules by collision with excited Hg atoms and the pressure of H_2, when the rate of production of excited Hg atoms is kept constant. It is shown to be in accord with Franck and Cario's experimental results, leading to a value for $\sigma^2\tau$ of $7.22\ 10^{-22}$, where σ is the distance between centers of H_2 molecules and excited Hg atoms at a collision and τ is the average duration of the excited state. Assuming σ to be of the order of magnitude of atomic diameters, τ is found to be about 10^{-7} sec. The equation derived here and a different one of Cario's are compared and the former found to be in better agreement with experiment. (2) *In mixtures with air, computed from diminution of the fluorescence by adding air,* found by R. W. Wood. The same theory is applied to the fluorescence experiments of Wood, assuming a constant rate of production of excited atoms, but the agreement is not good. The theory is extended to cover the possibility of successive impacts of the excited Hg atom, and the form of the relation is found to be the same in this case. It is found that the theory does accord qualitatively with the experimental data of higher pressures, indicating an increased rate of production of excited Hg atoms for the same illumination, and a smaller value of τ with air than with H_2.

Part I. The Dissociation of Hydrogen by Excited Mercury Atoms

CARIO AND FRANCK[1] have shown that when a mixture of hydrogen and mercury vapor is illuminated with light of wave-length 2536.7 from a mercury arc lamp, with copper oxide present, water vapor is formed. Their explanation of this phenomenon, which fits all of the experimental facts, is that the mercury atoms are put into an excited state by absorption of the light and then upon collision with hydrogen molecules give up their energy, dissociating the hydrogen molecules. Such collisions are called collisions of the second kind. The hydrogen atoms so formed readily react with the oxide to form water vapor. They made experiments on the rate of formation of water vapor for different pressures of hydrogen, the mercury vapor pressure and the intensity of illumination being kept constant. The water vapor was frozen out of the tube as it formed so that the rate of fall of pressure in the tube was a meas-

[1] G. Cario and J. Franck, Zeit. f. Phys. **11**, 161, 1922

ure of the rate of reaction. The data as taken from the experimental points indicated on the curve given in their paper are as in Table I.

TABLE I

Results of Cario and Franck[1]

Pressure of H_2	Rate of pressure drop
0.0101 mm Hg	$0.90(10)^{-4}$ mm/min.
0.0202	1.60
0.0300	2.14
0.0500	2.94
0.0855	4.00
0.1400	5.00

From these data it is possible to calculate an approximate value for the average life of the mercury atom in the excited state, as the following considerations show.

Let τ be the average life of an excited atom and T be the average time between successive collisions of a mercury atom with hydrogen molecules. Then assuming random distributions of lives of excited atoms and free times of excited atoms, the probability that the atom will remain excited a time t is $e^{-t/\tau}$; the probability that an atom will not collide in time t is $e^{-t/T}$; the probability that an atom will not collide in time $(t+dt)$ is $e^{-(t+dt)/T}$. The probability that the atom will collide in the time between t and $(t+dt)$ is the difference between the last two probabilities. Expanding and keeping only the term with dt to the first power, gives

$$e^{-t/T}-e^{-(t+dt)/T}=e^{-t/T}\,dt/T.$$

The probability that the atom will collide in the time between t and $(t+dt)$ while still in the excited state is the product of the independent probabilities for collision and duration in the excited state. It is

$$e^{-t/T}\,e^{-t/\tau}\,dt/T=e^{-(T+\tau)t/T\tau}\,dt/T.$$

The probability that an atom will collide while still excited is obtained by summing these probabilities for all values of t, that is, by integrating.

$$P=\int_0^\infty e^{-(T+\tau)t/T\tau}\,\frac{dt}{T}=-\frac{\tau}{T+\tau}\left[e^{-(T+\tau)t/T\tau}\right]_0^\infty=\frac{\tau}{T+\tau}.$$

For a given rate of production of excited mercury atoms the rate of reaction will be proportional to this probability. Let r represent the rate of reaction and C the constant of proportionality. Then

$$r=C\tau/(T+\tau).$$

According to the kinetic theory of gases T is inversely proportional to the pressure. In

$$pT=1/\sigma^2A$$

p is the pressure expressed in millimeters of mercury, σ is the distance between the centers of the excited mercury atom and hydrogen molecule at collision, and[2]

$$A = 2666.6 \sqrt{\frac{2\pi N}{k\theta} \frac{(m+m_1)}{mm_1}},$$

where N is the number of molecules per gram molecule, k is the gas constant per molecule, θ is the absolute temperature, m is the atomic weight of mercury, and m_1 the molecular weight of the hydrogen molecule.

The equation becomes

$$r = C\left(\frac{1}{1+1/A\sigma^2\tau p}\right) \tag{1}$$

which can be put in the form

$$\frac{1}{r} = \frac{1}{CA\sigma^2\tau} \cdot \frac{1}{p} + \frac{1}{C}$$

from which it is apparent that if this theory is correct we should, upon plotting values of $1/p$ for abscissas and $1/r$ for ordinates, obtain a straight line of slope $1/CA\sigma^2\tau$ and of $1/r$ intercept $1/C$. The quotient of the intercept by the slope will give $A\sigma^2\tau$.

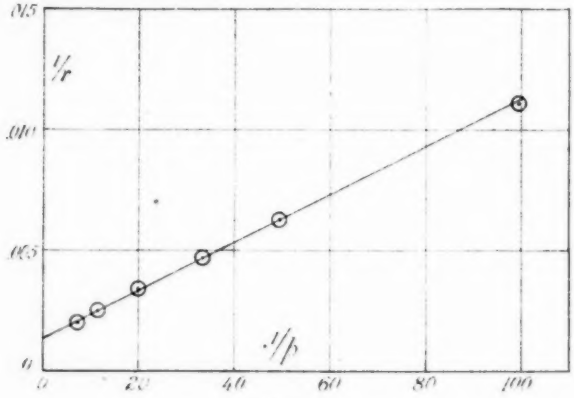

Fig. 1

Fig. 1 shows the line obtained by plotting the data of Table I in this manner. The values of the slope and intercept are 0.0000990 and 0.00130 respectively. Therefore

$$A\sigma^2\tau = 13.13$$

Using the following values of the constants: $N = 6.07\ (10)^{23}$; $k = 1.371\ (10)^{-16}$; $\theta = 318°$; $m = 200.6$; $m_1 = 2.016$; I find that

$$\sigma^2\tau = 7.44\ (10)^{-22}$$

Assuming σ to be 10^{-8} cm, $\tau = 7.44\ (10)^{-6}$ sec.; assuming σ to be 10^{-7} cm, $\tau = 7.44\ (10)^{-8}$ sec. The true value of τ probably lies between those

[2] G. Cario, Zeits. f. Phys. **10**, 185, 1922

two limits unless the effective size of the mercury atom in the excited state is quite large compared to its normal size.

In the derivation of Eq. (1) the possible effect of collisions of excited mercury atoms with normal ones has been neglected. The experimental tube was heated to 45° and connected to a liquid air trap so that the mercury vapor pressure was some value not far below 0.007 mm. The number of such collisions would not be negligible in comparison with the number of collisions with hydrogen molecules at the lower hydrogen pressures. The fact that the data agree with the simple theory in which collisions with other mercury atoms have been neglected would seem to indicate that although not negligible in number such collisions have a negligible effect. This means that the probability that an excited mercury atom will lose its energy upon collision with a normal mercury atom is very small. Experiments are being undertaken to obtain more information on this point.

It should be pointed out that this method gives the mean life of the atom in the $2p_2$ state and takes no account of the possibility of the atom being put into metastable $2p_1$ or $2p_3$ states by collision with hydrogen molecules. The result of such collisions is eventual reaction with hydrogen molecules and is quite the same for this experiment as if the reaction had taken place immediately at collision.

Cario[2] derives a similar equation, to explain the quenching of fluorescence of mercury vapor by air, using T as the time between successive collisions, but not using the probability of a free time t in a random distribution of free times. His equation is

$$z_2 = n(\tau/T)\ (1-e^{-T/\tau})$$

which, for application to this experiment, can be written

$$r = C'p\ (1-e^{-1/A\sigma^2\tau p}). \tag{2}$$

The values of the constants C' and $A\sigma^2\tau$ can be calculated as follows. If $p_2 = 2p_1$

$$\frac{r_1}{r_2} = \tfrac{1}{2}\,\frac{(1-e^{-2/A\sigma^2\tau p_1})}{(1-e^{-1/A\sigma^2\tau p_1})} = \tfrac{1}{2}\ (1+e^{-1/A\sigma^2\tau p_1}).$$

Using the two points from the experimental curve $p_1 = 0.070$, $r_1 = 3.55(10)^{-4}$; $p_2 = 0.140$, $r_2 = 5.00(10)^{-4}$, I find that $A\sigma^2\tau = 8.25$ and $C' = 61.6(10)^{-4}$. Eq. (2) becomes

$$r = 61.6\ (10)^{-4}\ p(1-e^{-1/8.25p}).$$

Using the same two points to calculate the constants, Eq. (1) becomes

$$r = 8.51\ (10)^{-4}\ \frac{1}{1+1/10.18p}.$$

With these two equations I have calculated the values of r for different pressures and have plotted these points and the experimental ones in Fig. 2. Eq. (1) seems to fit the experimental data better.

Part II. The Diminution of the Fluorescence of Mercury Vapor by Admixture of Air

Cario developed his equation in connection with a discussion of experiments upon the fluorescence of mercury vapor by R. W. Wood.[3] Wood found that the resonance radiation fluorescence of mercury vapor was decreased by the admixture of air and made measurements of the

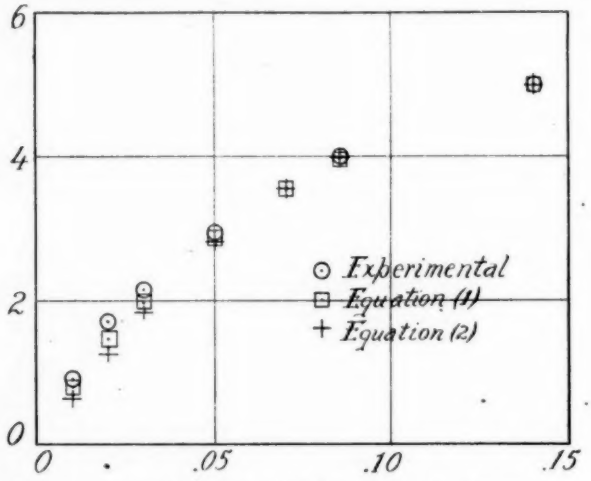

Fig. 2. Rate of reaction $r(10)^{-4}$ as a function of pressure.

fluorescence for different pressures of air. Cario explains this as being due to collisions of the second kind which permit the atoms to return to the normal state without radiating. If this is the correct explanation the intensity, according to the theory developed above, should be given by the equation

$$I = I_0 \left(1 - \frac{k}{1+1/A\sigma^2\tau p}\right),$$

in which I = intensity, I_0 = intensity at zero pressure, k = the probability that a collision will cause the atom to lose its energy without radiating. Re-writing the equation

$$\frac{1}{I_0 - I} = \frac{1}{kI_0} \cdot \frac{1}{A\sigma^2\tau} \cdot \frac{1}{p} + \frac{1}{kI_0}$$

shows that as above a straight line should be obtained by plotting values of $1/p$ for abscissas and $1/(I_0-I)$ for ordinates. Table II gives Wood's

[3] R. W. Wood, Phil. Mag. **23**, 689, 1912 and Phys. Zeits. **13**, 353, 1912

data and Fig. 3 the curve obtained. It is far from being a straight line. Cario's equation does not fit the data well, either, and his numerical results obtained by its use are of little significance.

TABLE II

Data of R. W. Wood[3]

Air pressure	I	(I_0-I)
0.01 mm	300	0
0.45	230	70
1.10	200	100
2.20	170	130
6.20	100	200
9.50	70	230
14.20	50	250
18.00	40	260
32.00	12	288

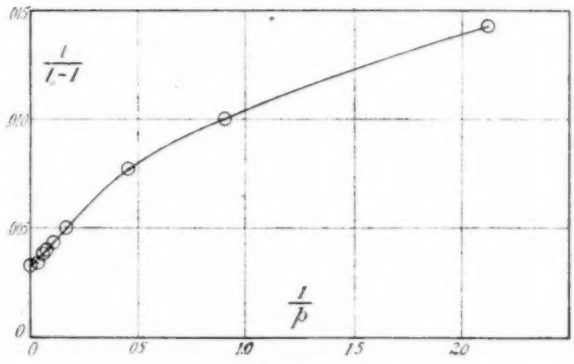

Fig. 3

It seemed that it might be possible to explain the discrepancy as being due to the neglect of the possibility of several successive collisions of excited mercury atoms with air molecules before their return to the normal state by radiation or a collision of the second kind. Assume that the probability that a mercury atom will upon collision undergo a radiationless transition to the normal state is k, and that the probability that it will survive the collision unchanged is a. The probability that it will radiate at collision is then $(1-k-a)$, since that seems to be the only other possibility. The number of excited atoms produced is proportional to I_0, the fraction of them undergoing collisions of the second kind at the first collision is $k\tau/(T+\tau)$, the fraction unchanged at the first collision is $a\tau/(T+\tau)$, the fraction undergoing collisions of the second kind at the second collision is $ka\tau^2/(T+\tau)^2$, etc. The equation for I is

$$I=I_0\left\{1-\frac{k\tau}{T+\tau}\left[1+\frac{a\tau}{T+\tau}+\frac{a^2\tau^2}{(T+\tau)^2}+\ \cdots\right]\right\}$$

Using the fact that $1/(1-x)=1+x+x^2+x^3+\ldots$ the equation can be written

$$I=I_0\left\{1-\frac{k\tau}{T+\tau}\left(\frac{1}{1-a\tau/(T+\tau)}\right)\right\}=I_0\left\{1-\frac{k\tau}{T+(1-a)\tau}\right\} \quad (3)$$

which after rearrangement and substitution becomes,

$$\frac{1}{I_0-I}=\frac{1}{kI_0}\left\{\frac{1}{A\sigma^2\tau}\cdot\frac{1}{p}+1-a\right\}.$$

The equation is again that of a straight line for values of $1/p$ and $1/(I_0-I)$, although the interpretation of the constants is different. Eq. (3) can be put in the form

$$\frac{1}{I}=\frac{1}{I_0}\{1+(1-a)\,A\sigma^2\tau p\}\left\{\frac{1}{1+(1-k-a)\,A\sigma^2\tau p}\right\}$$

which suggests plotting corresponding values of p and $1/I$. The curve so obtained is shown in Fig. 4. The experimental error in determining I is relatively most important for the point $p=32$, $I=12$, (not plotted)

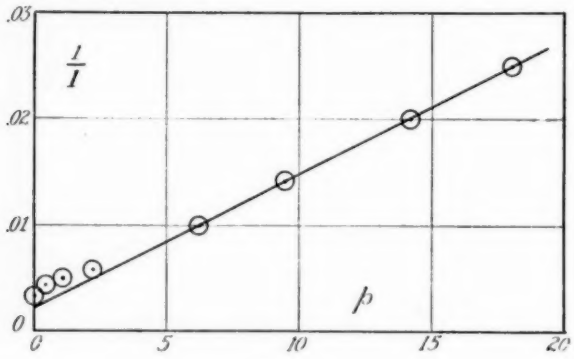

Fig. 4

and may well explain its deviation from a value which would fall in with the others according to any regular law. A straight line can be drawn through the four other high pressure points. If this is considered to be significant the following conclusions can be drawn. $1-k-a$ must be negligibly small, for the term containing it as a factor would be of importance at higher pressures. The intercept is 0.00238 which gives a value for I_0 of 420, whereas the I measured by Wood at very low air pressures was only 300. This indicates that the rate of production of excited mercury atoms is increased by the presence of the air. The quotient of the slope by the intercept which gives $(1-a)\,A\sigma^2\tau$ is 0.534. Computing A with the proper values of the temperature and the molecular weights, $(1-a)\,\sigma^2\tau$ is found to be $7.2\,(10)^{-23}$. The value obtained for the hydrogen

experiment was 7.4 $(10)^{-22}$. Since σ is probably larger with the air it would seem that $(1-a)$ must be a small fraction or that τ must be smaller with air.

The evidence is hardly sufficient to warrant attaching much importance to these conclusions, but the value and need of new experimental work is shown. The fact remains that the equation represents the data at higher pressures. That the rate of production of excited atoms should increase with the air pressure is consistent with other experiments performed by Wood and discussed in the same paper. He found that the absorption line was broadened by the admixture of air but that the absorption for the very homogeneous light emitted by the fluorescing mercury vapor in his so-called resonance lamp was decreased. The simplest interpretation of these results is that many of the atoms are so affected by the fields of the neighboring air molecules that they are unable to absorb light of the same wave-length as if they were unaffected, but can absorb light of a wave-length slightly different. The total absorption in a thin layer would, then, be the same for a given intensity but the diminution of intensity of the beam as it passed through the vapor would be less for any particular narrow region of wave-length and therefore less for the beam as a whole. Wood[4] has shown by direct experiment that the admixture of He has this effect.

It seems as if more reliable information can be obtained by working with single gases, by the chemical method, at low pressures at which the disturbing effects would be small. Experiments of that sort are being carried out. In conclusion, I wish to thank Professor K. T. Compton for his valuable criticism and suggestions.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
October 26, 1923

[4] R. W. Wood, Phil. Mag. **44**, 1107, 1922

THE PHOTOLUMINESCENCE OF FLAMES. II

By E. L. Nichols and H. L. Howes

Abstract

Photoluminescence of salted flames.—Study of a *new flat hydrogen flame* showed that the sensitiveness to excitation noted in previous work, is confined chiefly to the boundary between the oxidizing and reducing regions. When excited by exposure to light from an amalgam arc, measurements of the positions of the edges of the bands and of the intensities of the maxima and minima showed that the effect of excitation was to decrease the width of the bands and to increase the sharpness and the intensity of the maxima, for *flames salted with Ba, Ca and Sr. In the case of Tl*, the green line was increased in brightness more than 50 times. This effect was traced in the presence of Tl in the arc, and by dispersing the light so as to use only narrow spectral regions, it was found that the Th lines 5351, 3776 and 3519 A excite the flame, whereas neighboring mercury lines are inactive. The luminescence is thus shown to be selective and to be closely analogous to the so-called resonance radiation of vapors.

IN a recent paper the present authors[1] described observations upon the photo-luminescence of hydrogen flames containing salts of Li, Na, Ca, Sr. and Ba. Measurements of the changes in brightness of the emission bands under various conditions of excitation were also given.

Similar results have since been obtained with Rb, Cs and Tl and many further experiments have been made to ascertain the best form of flame, to study in detail such changes, in addition to the increased brightness, as may occur in the individual bands and to determine the effects of selective excitation.

Our study of flames led ultimately to the adoption of the form shown in Fig. 1 in which A is an ordinary acetylene burner (of steatite) supplied from a tank of compressed hydrogen. Air containing finely divided spray from a solution of the salt to be used was carried from the aspirator (not shown) to the immediate proximity of the air ducts of the burner through the tubes T, T, whence it was drawn into the flame. A further supply of impregnated air from the same aspirator was delivered to the outer face of the flat flame F, through narrow longitudinal slots in two tubes L, L, mounted horizontally and parallel to the faces of the flame near its base. In this way the salt is conveyed simultaneously to the body and to the surface layers of the flame, with better results than when the spray is introduced into the hydrogen gas before the latter enters the burner.

[1] Nichols and Howes, Phys. Rev. (2), **22**, 425, November 1923

Changes in the Flame Spectra

The source of excitation selected for use in most of the experiments to be described in this paper, was an "amalgam arc" in quartz. This source of radiation has the following good qualities. It is weak in the quenching rays of the red, rich in the violet and ultra-violet, and reasonably steady.

When one of the flames under consideration is excited by such an arc or by any source capable of producing luminescence, and is studied by means of a spectro-photometer, as in our earlier experiments, an observer at the eyepiece is aware of certain rather obscure changes in the appearance of the spectrum.

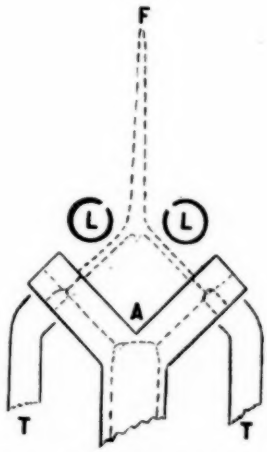

Fig. 1. Form of flame adopted.

The increase in brightness may not be immediately obvious; changes of intensity, indeed, can best be studied by removing the eyepiece and balancing the contrast field of the instrument. With sodium or lithium in the flame there is of course little else to observe, at least with the dispersion afforded by a single prism. One is, however, aware of a change when the shutter between the arc and the flame is opened. The line-like band becomes sharper as to its edges and the dim background, however free from stray light, becomes blacker when the flame is illuminated.

It seems probable that we have to do with changes in the structure of the band, similar to those described by Strutt[2] in his experiments upon sodium vapor in vacuo, but these were quite beyond the power of the constant deviation instrument at our command.

The broader bands in the spectra of calcium, strontium and barium afford an easier field. Appreciable shifts of the edges occur on excitation

[2] Strutt, R. J., Proc. Royal Soc. **96,** 272 (1920-21)

and various structural changes may be perceived. Observations of these effects were made throughout the visible spectrum, and the results are indicated in Figs. 2, 3 and 4. In these diagrams the bands are lettered A, B, C etc, beginning at the red end of the spectrum, and the customary

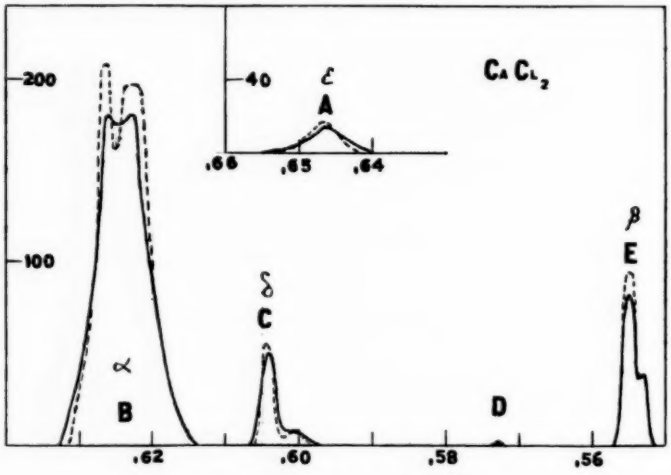

Fig. 2. Spectrum of calcium flame.

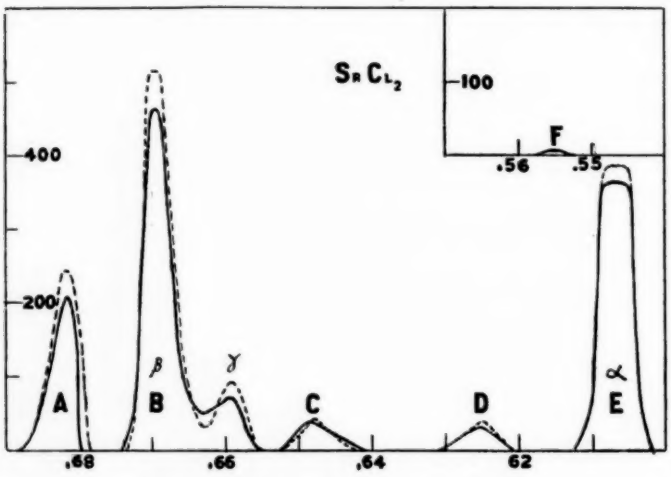

Fig. 3. Spectrum of strontium flame.

designations α, β, γ, etc., as used in spectrum analysis, are added. The various bands are drawn in solid lines and the changes brought about by exposure to the exciting light are shown by broken lines.

Measurements upon which to base these sketches were made as follows: (1) Edges, crests and the depressions between crests, when such were perceptible, were located before and during excitation. (2) The bright-

ness of each crest and the amount of light in the depressions were estimated before and during excitation.

It will be seen from the figures that the movement of the edge of a band upon excitation is nearly always inward so as to produce an effect of narrowing, and that the change occurs chiefly at the tail of the band rather than on the steeper slope (see particularly in this regard the three bands E, F, G, in the spectrum of barium, Fig. 4, all of which tail off in a similar manner towards the red). The unsymmetrical narrowing gives the impression of a shift of the band, but it will be noted that the crests

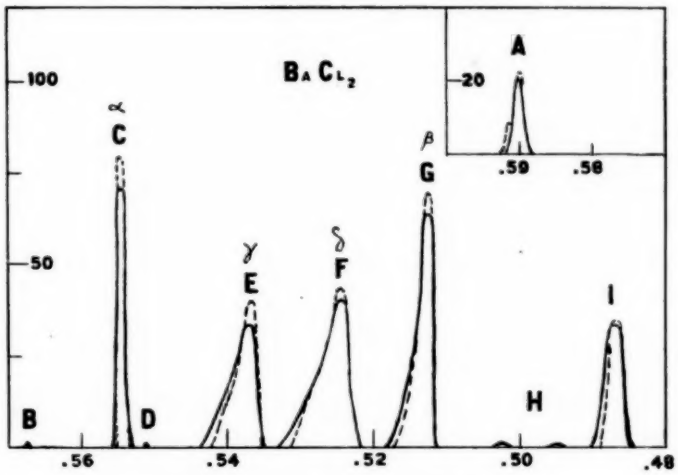

Fig. 4. Spectrum of barium flame.

are not shifted perceptibly by excitation. They are increased in intensity however and the depressions between crests (see bands B and C in Fig. 2 and B in Fig. 3) are deepened, but also without shift.

This deepening of the depressions is one of the striking effects of excitation. The existence of a depression in a broad crested band, and of the accompanying resolution of the band into the two components of which it consists sometimes becomes evident only when the flame is exposed to the exciting light.

All crests are enhanced during excitation, and in nearly equal proportions. Comparison of bands where observations were not simultaneous are of doubtful value in this respect because of the fluctuating sensitiveness of these flames, but to watch the sudden outcropping of the left hand crest of band B or of band E in the spectrum when a calcium flame is exposed to light is to be convinced of the selective character of the effect.

Regions of Photo-Luminescent Sensitiveness

In our preliminary paper the statement was made that the photo-luminescence depended upon the conditions of combustion. In these later experiments, in which an image of the flame was focussed sharply upon the slit of the spectro-photometer, and in which we were able to explore the flame laterally, a more specific result was obtained. It was then found that the sensitiveness to excitation was chiefly confined to certain narrow layers of the flame, and particularly to the boundary between the oxidizing and reducing regions.

In other words the sheath surrounding the main body of the flame, which is most active in producing luminescence when brought in contact with various oxides is also the chief seat of the photo-luminescence of the flame itself.[3] Turbulence, which tends to destroy the integrity of this boundary, is therefore detrimental to the effect, whereas certain quietly-burning flames have been found peculiarly sensitive.

The Thallium Flame

A flame impregnated with spray containing thallium chloride and exposed in the usual way to the light of the amalgam arc showed an extraordinary and unlooked for activity. When the shutter was open the green line of thallium was increased in intensity over fifty per cent and in some subsequent trials over fifty times, an effect which was striking whether viewed directly through the eyepiece of the spectrophotometer or indirectly by use of the contrast field of the Lummer-Brodhun prism.

The very great activity of this particular flame was finally traced to the unsuspected existence of thallium in the mercury of the arc lamp and to the consequent presence of the powerful lines of that element at 5350.7, 3775.9 and 3519.4 A. Although owing to the small amount of thallium in the amalgam these lines did not compare in brightness with the neighboring lines of mercury, they were easily visible, the green line directly and the ultra-violet lines by the aid of a fluorescent screen. Interposition of a plate glass screen one centimeter in thickness did not diminish the excitation appreciably, hence it was inferred that the effect was not due to the action of the far ultra-violet. A glass transmitting the violet and near ultra-violet but opaque to the green line, gave a somewhat reduced excitation while a filter opaque to all beyond the green weakened the effect still more. From these observations it seemed that the lines at 5350, 3776 and 3519 were jointly responsible for the photo-luminescence of the flame.

[3] Nichols and Wilber, Phys. Rev. (2) **17**, 453 (1921)

To put this conclusion upon a still more definite basis, the slit was removed from a large Hilger quartz spectrograph and the contracted portion of the quartz tube of the amalgam arc, which has a diameter of about 3 mm was mounted in its place. In this way any desired portion of the visible or ultra-violet spectrum could be focussed within the hydrogen-thallium flame. The principal lines of the amalgam arc were sufficiently separated in this spectrum to permit of their use individually for excitation.

Although the effects obtained by this method were much smaller than when the undispersed light of the arc was used, the results were perfectly definite and decisive. It was found that while the intense mercury lines at 4359 and 3126 produced *no excitation whatever* (the average, of sets of readings of the intensity of the thallium line 5350 with and without exposure being identical), the region containing the thallium lines 3776 and 3519, enhanced the green line by about 7 per cent, two sets of readings giving respectively 7.6 and 6.8 per cent. The line at 3776 taken alone, the adjoining mercury line at 3650 and the thallium line at 3519 being excluded, gave 3.1 per cent excitation. The region of the visible spectrum containing the green line at 5350 itself excited the flame feebly but definitely (1.4 per cent).

These results with thallium would seem to be related very intimately with those on the excitation of sodium vapor by means of the D lines and the 303 line of sodium recently described by Strutt.[2] The effect may thus be designated as resonance radiation in the broader sense in which that term is frequently used[4] but not in the restricted sense proposed by Franck. The narrowing of the bands by exposure of the flame to the exciting light is however a matter which demands further experimental study.

DEPARTMENT OF PHYSICS,
CORNELL UNIVERSITY,
October 30, 1923.

[4] See Foote and Mohler, Origin of Spectra, p. 90

THE EFFECT OF TEMPERATURE ON THE LUMINOSITY OF RADIUM COMPOUNDS

By Jessie A. Rodman

Abstract

Effect of temperature on the luminosity of $RaBr_2$ and of mixtures with $BaBr_2$. —(1) In the case of pure $RaBr_2$, a tube containing 9 mg after heating to 600°C gave an initial luminosity of 5600° μ-candles/cm^2 which decreased in 1 hr to 3600 or 2800 according as the tube was cooled to 20° suddenly or gradually, and continued to decrease, according to the equation $I_t = I_\infty + I_0 e^{-At^{.67}}$, reaching an equilibrium value of only 6μ-c/cm^2 after 500 hours. This equilibrium value increases somewhat with the temperature but depends only on the temperature and not on the previous treatment. (2) In the case of mixtures with $BaBr_2$, the initial luminosity after removing from the furnace increases exponentially with the temperature; the rate of decay is greater the lower the temperature at which the sample is held; the equilibrium luminosity for 1 to 3 per cent $RaBr_2$ at 20° increases markedly as the radium content decreases and for higher temperatures decreases as the temperature is increased. For 7 per cent $RaBr_2$, however, the equilibrium luminosity at 20° is less than for either 3 or 100 per cent, and it increases with the temperature. In all cases, however, the equilibrium value depends only on the composition and on the temperature at which it is kept. These results are consistent with the suggestions by Rutherford of the formation of "active centers."

I. Introduction

SYSTEMATIC investigation of luminous compounds was undertaken first in 1910 by Marsden[1] who found that alpha particles from an emanation tube bombarding zinc sulfide imparted to it a luminosity that decreased more rapidly than the emanation causing it. Rutherford[2] explained this phenomenon by the presence in the zinc sulphide of active centers whose destruction was accompanied by the emission of light. According to this theory, (1) the brightness of the compound was dependent on the rate of destruction of these active centers, (2) the brightness decay followed an exponential law, and (3) the brightness should ultimately reach a zero value.

Patterson, Higgins and Walsh,[3] experimenting in the National Physics Laboratory in London, found that the luminosity decay curves of zinc sulfide, although exponential for the first part of the life of the compounds, approached a constant value, and that the luminosity never would become zero. To explain this, Walsh assumed that while active centers were being destroyed, others were being formed, and that equilibrium

[1] Marsden, Proc. Roy. Soc., A **83**, 548–561, (1909–10)
[2] Rutherford, Proc. Roy. Soc., A **83**, 561–572, (1909–10)
[3] Patterson, Higgins and Walsh, Proc. Phys. Soc. Lon., **19**, 215–249, (1916–17)

luminosity occurred when the destruction rate equalled the formation rate. No effort was made to determine upon what factors the formation rate depended.

Kabakjian began in 1918 work on a new group of luminous compounds, radium bromide and barium bromide, and found that they possessed the extraordinary property of complete rejuvenation of luminosity on the application of heat. With Karrer,[4] he undertook a systematic investigation of these compounds, which was interrupted by war conditions. The object of the present investigation is to continue this work, to investigate the luminosity decay curves of pure radium bromide and of mixtures of radium bromide and barium bromide, and to show that each compound has a definite equilibrium luminosity which is a function of the temperature at which the compound is kept.

II. Method of Measurement

Five tubes were used, especially prepared by Kabakjian in such a manner as to show extremely high luminosity. The contents of the tubes are indicated in Table I.

TABLE I

Contents of tubes under investigation

Tube	$RaBr_2$ (x)	$BaBr_2$ (y)	$100x/(x+y)$
1	9.0 mg	0 mg	100
2	0.735	19.265	3.7
3	1.41	18.59	7.1
4	1.27	76.76	1.6
5	1.01	62.41	1.6

The compounds were fused in pyrex glass tubes and the tubes sealed under reduced pressure. Tubes of high radium content were used since it was found that the rate of luminosity decay was proportional to the radium content, hence the higher the content the shorter the period necessary for the investigation of any one factor.

For heating the tubes, an electric furnace, cylindrical in shape, having a heating chamber with a uniform temperature zone about 10 cm long and 2 cm in diameter was used. The temperature was measured by a quartz-enclosed platinum-rhodium thermometer and a Thwing pyrometer. A brass cylinder with cylindrical holes large enough to admit the radium tubes was used as container. This was placed in contact with the thermocouple case so that the temperature recorded by the instrument might be taken as the temperature of the radium itself. Five minutes heating in the furnace was sufficient to bring the tube to equilibrium.

[4] Karrer and Kabakjian, Jour. Franklin Inst. (Sept. 1918)

Tube luminosities of sufficient magnitude were measured by means of a Nutting polarization photometer manufactured by Hilger and obtained from the Arthur H. Thomas Co. of Philadelphia. The optical system is indicated on the right in Fig. 1. In making an observation, the telescope is focused on the photometer cube so that the field appears as two strips of reflected light from the radium with the transmitted light from the reference lamp between them. By varying the intensity of the reference lamp by means of the Nicol prism B″, the strip is made alternately lighter and darker than the strips illuminated by the radium until a color match is obtained.

The arrangement of apparatus is shown in Fig. 1. The reference lamp L is fed by storage batteries and maintained by a variable resistance at a definite constant voltage, indicated by the voltmeter V. The lamp is

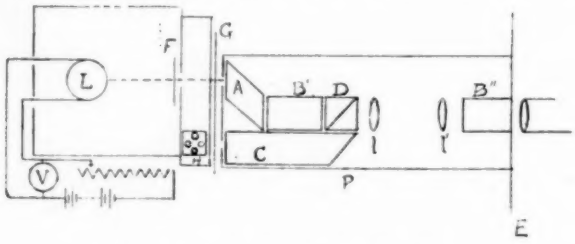

Fig. 1. Arrangement of apparatus.

H—Carbon block containing tube under observation	
A, C—Reflecting prisms	B', B''—Nicol prisms
D—Photometer cube	E—Disk graduated in I_s/I_r
l, l'—Lenses.	G—Ground glass screen

mounted on guides so that its illumination of the screen may be controlled by changing its distance from the screen as well as by changing the voltage across the lamp. Light from L falls upon the ground glass diffusing screen G after passing through the green gelatine filter F which is interposed to produce a better color match. The radium rests in a carbon block mounted on a slide immediately in front of the diffusing screen.

To determine the candle-power of the reference lamp, it was compared by means of a Lummer-Brodhun photometer with a carbon lamp standardized by the Bureau of Standards. Its candle power when operated at 80 volts was found to be 0.27; when operated at 90 volts, 0.70.

To determine the absorption of the green filter, the luminosity of a radium tube was measured with and without the green filter between the reference lamp and the photometer. The ratio of the two intensities was taken as the transmission coefficient under the conditions of use. The Purkinje effect is operative for intensities of light comparable with that of the radium, but measuring the transmission coefficient under

conditions identical with those under which the luminosity measurements were made, eliminated as far as possible errors due to this effect. Since the transmission coefficient depends on the wave-length of the light transmitted, and since the color of the light emitted by the reference lamp at 80 volts was markedly different from that emitted by the lamp when it was operated at 90 volts, the transmission coefficient of the screen was determined under both conditions.

To maintain the radium at constant temperature during photometric measurements, it was placed in a carbon block, insulated, and supplied with a convenient system of heating coils controlled by a thermometer thermostat. The slide on which the block rested was covered with a sheet of copper as was the surface of the lamp box to which the slide was attached. This increased the radiating surface and prevented charring of the wood.

The brightness of the tubes was readily calculated from the scale readings of the photometer and the constants of the apparatus. The photometer is graduated in logarithms of the ratio of the illuminating power of the reference lamp to that of the radium tube. If, then, K is the transmission coefficient of the filter, C_1 the candle-power of the reference lamp, C_2 the apparent candle-power of the radium tube, d_1 and d_2 their respective distances from the ground glass screen,

$$\log_{10}(KC_1/d_1^2) - \log_{10}(C_2/d_2^2) = \text{scale reading} = X.$$

If A is the area of the exposed luminous portion of the tube, the brightness B in apparent candle-power per square centimeter is

$$B = (KC_1d_2^2)/(d_1^2\, 10^X\, A).$$

Measurements of tube luminosity below the scope of the instrument were made by means of a 'radium scale.' This is a series of eight tubes carefully graded in radium content so that when heated to 500° they exhibit luminosities ranging from 'just visible' to 10 microcandles per square centimeter. The brightness of the most luminous one was determined photometrically. By comparison with these the approximate luminosity of low intensity tubes could be determined. For quantitative work the scale is of little value; it is possible, however, by its use to determine with a high degree of certainty whether or not a tube has reached a definite equilibrium value.

III. Experimental Procedure and Results

1. *Determination of time-luminosity curves.* To determine the time rate of decay of luminosity of a tube at a given temperature θ, the tube was heated to any desired temperature θ_0, then allowed to cool to the required temperature θ and maintained at that temperature. Its lumin-

osity was read at half to one hour intervals for the first day, at longer intervals on succeeding days. Experimental results for typical time-luminosity curves of tubes 1 and 2 are given in Fig. 2.

Analysis of curves for tubes 1, 2, and 3 for temperature limits 600° – 20° C taken in this way, shows that (1) the initial luminosity of c.p. radium bromide is many times that of mixtures of radium bromide and barium bromide; (2) the initial luminosities of the mixtures are almost

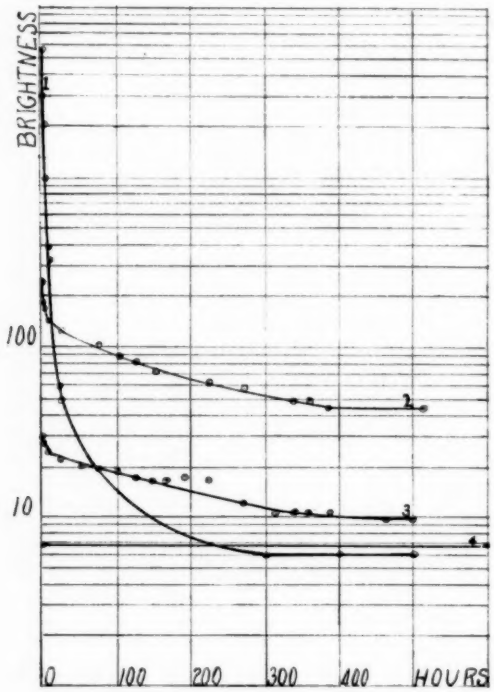

Fig. 2. Time-luminosity curves

Curve	Tube	Initial temperature	Temperature of observation
1	1	600° C	20° C
2	2	600	20
3	2	600	150
4	2	150	150

directly proportional to the per cent of radium bromide present; (3) the rate of decay was much greater for c.p. radium bromide than for the mixture, but that the luminosity decay curves were of similar form for all the tubes investigated; (4) each tube reached an equilibrium luminosity that varies in inverse order with the radium bromide content.

An empirical formula for the variation in luminosity with time was obtained from consideration of a typical time-luminosity curve for

log log $I_0/(I_t-I_\infty)$ plotted against log t (see Fig. 3). After the first hour, the curve is a straight line which may be represented by the equation:

$$I_t = I_\infty + I_0\, e^{-At^B}$$

For example, for tube No. 1 (initial temperature 600° C; temperature of observation 20° C) we have

$$I_t = 6 + 6960\, e^{-.267t^{.67}} (\mu c/cm^2),$$

where t is in hours.

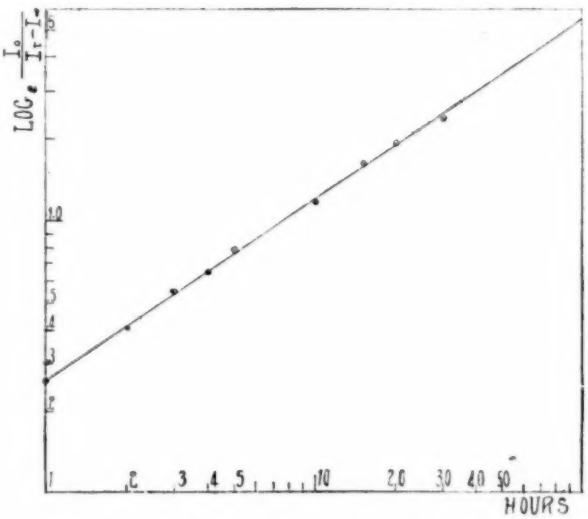

Fig. 3. Time-luminosity curve for tube 1.
I_0—Intensity of the reference lamp
I_t—Intensity of the radium light

2. *Factors affecting initial luminosity.* Further investigation of the factors affecting initial luminosities of the tubes made it apparent that the initial luminosities were reproduced at will provided that certain conditions were exactly reproduced. The controlling conditions were found to be (1) the initial temperature of the tube; (2) the rate at which it was cooled.

(1) The effect of initial temperature on initial luminosity was studied with tube No. 2. The luminosity of this was measured at 18° C, after it had reached equilibrium value. The tube was then heated to 260° C or some higher temperature and the luminosity measured five minutes after removal from the furnace. The results appear in Curve 1 of Fig. 4, in which the initial luminosity is plotted against temperature. The drop in luminosity at 690° is due probably to escape of emanation at that temperature.

On plotting on semi-logarithmic paper initial luminosity against temperature (Curve 2, Fig. 4), a straight line is obtained. This indicates that the curve may be represented by the empirical equation

$$I_\theta = 1.85\ e^{1.56\theta}$$

in which θ is the temperature centigrade.

(2) The effect of rate of cooling is illustrated by the observations on the c.p. $RaBr_2$ tube No. 1. This tube was heated to 600° C, permitted to cool at various rates, and observed one hour after removal from the

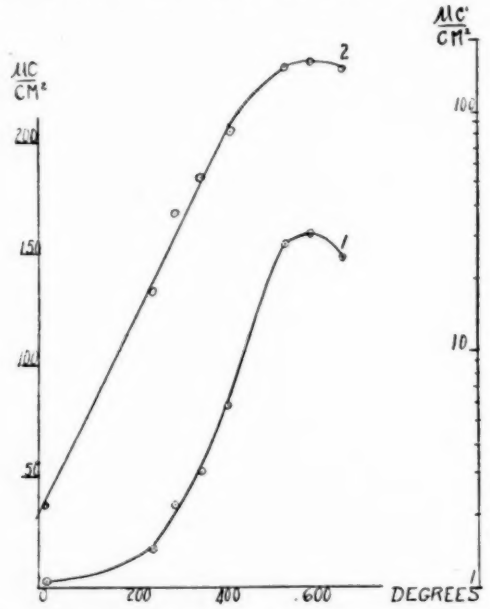

Fig. 4. Initial luminosity at various temperatures for tube 2.
Curve 1 is based on the left hand scale, Curve 2 on the right hand scale.
Luminosity was measured 5 min. after removal from the furnace.

furnace. The results are cited in Table II. It is seen that when cooled in 2 min. the luminosity is nearly 30 per cent greater than when cooled in 30 min. Similar results were observed in tubes 2, 3, 4 and 5, but were not measured photometrically.

TABLE II

Effect of rate of cooling on luminosity of pure $RaBr_2$

Initial temperature 600° C; temperature of observation 20° C

Time of cooling	Brightness 1 hour after removal from furnace
2 min.	3610 μc/cm²
5	3480
10	3210
20	2830
30	2800

3. *Equilibrium luminosity.* The time-luminosity curves for temperature limits 600-20° showed that each tube reached an equilibrium luminosity dependent on the compound used. Other curves for temperature limits 600-100° and 600-150° showed that the equilibrium luminosity of each tube is dependent on the temperature at which the tube is kept. In order to investigate the possible effect of previous history on equilibrium luminosity of a tube at a given temperature, tubes No. 2 and No. 3, having decayed to equilibrium luminosity at 20° C were heated to 100°C and the time-luminosity curves taken at that temperature. The equilibrium luminosity so measured agreed in each case with that obtained by the previous method for the same temperature. The equilibrium luminosities at 150° C obtained by the two methods also agree, as indicated in Table III. *The equilibrium luminosity of a tube is dependent, therefore, on the content and temperature of the tube only,* and is independent of the previous history of the tube. Table III summarizes the experiments on equilibrium luminosity for tubes No. 2 and No. 3.

TABLE III

Summary of the Experiments on Equilibrium Luminosity.

Initial temperature	Temperature of observation	Equilibrium luminosity ($\mu c/cm^2$)	
		Tube 3	Tube 2
600° C	20° C	1.0 $\mu c/cm^2$	45
600	100	2.21	12.5
600	150	6.9	6.9
100	100	2.2	12.5
150	150	6.9	6.9

The equilibrium luminosity of pure radium bromide varied much less for temperature changes within the range of temperatures used than the tubes containing a mixture of radium and barium bromides. On heating it to 100° and 150° respectively, slight increases in luminosity were observed but were of insufficient intensity for photometric measurement. Its behavior in this respect was similar to that of tube 3 containing 7 per cent radium bromide. Tube 2 of lower radium content exhibited a marked decrease in luminosity with increased temperature, a property displayed also by tubes of still lower radium content. An extended investigation of a large number of tubes of carefully graded radium content, when subjected to wide range of temperatures, is necessary to establish the luminosity-temperature-content relation. This involves measurement of much lower luminosities than the method described in this paper permits. A more flexible method is being developed that, it is hoped, will make possible the measurements required.

4. *Rate of decay.* A limited investigation of the effect of low temperatures on the rate of decay of luminosity of these compounds showed that

decreased temperature causes an increase in rate of luminosity decay. Two tubes, No. 4 and No. 5, prepared from the same mixture and therefore identical in composition, were heated to 600° C, cooled to room temperature and their luminosity measured. One tube was then placed in liquid air and the other maintained at room temperature. After nineteen hours the luminosity of the tube kept at room temperature had decayed to 83 per cent of its maximum value, and that of the tube kept at liquid air temperature to 68 per cent of its maximum value. Both tubes were reheated to 600° C and the process repeated with the tubes interchanged. Similar results were observed.

5. *Effect of subsequent heating on the luminosity of tubes.* Tubes (No. 4 and No. 5) heated to 600°, cooled suddenly to 20°, and subsequently heated successively to eight temperatures ranging from 40° to 218°, decreased in brightness as their temperature was raised. While being measured, the luminosities of the tubes would decay somewhat, but any errors caused by such normal decay during the five hours required for these measurements would not exceed 3 per cent of the maximum luminosity. The decrease in luminosity was only temporary as the tubes regained their brightness on being cooled to room temperature. Table IV gives the experimental results for tube No. 4. Those for tube No. 5 were similar.

TABLE IV

Effect of subsequent heating on luminosity of tube No. 4

Temperature of observation	Brightness
25° C	150 $\mu c/cm^2$
50	110
75	78
100	51.5
125	31.5
150	18.0
175	10
200	5

IV. DISCUSSION

As a result of this investigation certain facts are established that suggest the following explanation of the phenomenon.

It is evident that heating radium bromide to a sufficiently high temperature and cooling it, imparts to it the property of becoming luminous under bombardment of the alpha particles which it emits. Barium bromide heated and exposed to alpha particle bombardment also becomes luminous. For a given quantity of radium bromide the initial luminosity obtained from c.p. radium bromide is very much greater than that obtained from mixtures of the two bromides, but mixtures of the salts possess a relatively high equilibrium luminosity at the temperatures of observation.

If we assume that the luminosity in both cases is due to so-called active centers or unstable configurations, as Rutherford suggested in the case of zinc sulfide, it is evident that these active centers are formed on the absorption of heat energy by the compound. High temperatures followed by rapid cooling are necessary for the formation of any considerable number of them. Thermal agitation at high temperatures makes possible the instantaneous existence of large numbers of unstable configurations. Rapid decrease in agitation, incident to rapid cooling makes the instantaneous configuration permanent, other conditions remaining constant, in much the same way that rapid cooling produces crystalline steel, but gradual cooling permits the formation of a more stable form. The disintegration rate at any instant is proportional to the number of active centers present. If the luminosity of a tube depends on the rate of disintegration, it follows that rapid cooling, increasing the number of active centers present, would increase the luminosity of the tube as found in the experiments.

Maximum luminosity occurring when the tube was heated to 600° C and cooled suddenly to 20° C indicates that maximum number of active centers was formed. On subsequent heating the luminosity decreased due to the fact that increased thermal agitation decreased the susceptibility of the active centers to disintegration by alpha particle bombardment. It is probable that the active centers were not destroyed since no light was evolved as the temperature was raised.

That any one tube at a given temperature attains an equilibrium luminosity characteristic of that temperature, and never reaches zero luminosity, seems to indicate that active centers are produced at all temperatures, in numbers varying with the temperature. When the number of such centers produced at a given temperature is equal to the number destroyed, the luminosity becomes constant. According to this view, if the tubes were kept at absolute zero, the luminosities would disappear in time. This is in keeping with the fact that maintaining the compound at the temperature of liquid air considerably accelerated the decay in luminosity, due probably to the fact that very few active centers can be produced at that temperature.

In conclusion the writer wishes to express her most sincere appreciation to Dr. D. H. Kabakjian at whose suggestion and under whose direction the work was carried out, and to Dr. Horace C. Richards for his interest and many helpful suggestions.

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May 29, 1923.

COMPRESSIBILITY OF THE ALKALI HALIDES

J. C. SLATER

ABSTRACT

Compressibility of eleven alkali halides and its variations with pressure and temperature have been determined by measurements by Bridgman's new method, up to 12,000 atm. for both 30° C and 75° C. The samples were all single simple cubic crystals each grown from the melt in a new way, described elsewhere. The error in the values of the compressibility at zero pressure, κ_0, is probably less than one per cent; in the values for variation with pressure, ψ_0, and temperature the error may be 5 and 20 per cent respectively. By extrapolation approximate values of κ_0 for absolute zero are found. *Periodic relations.* Both κ_0 and ψ_0 when plotted against the alkali ion for a series of salts of the same halogen ion, or vice-versa, show similar behavior. The curves break sharply at the ion similar to argon (K or Cl) the rate of increase suddenly decreasing. This behavior is also shown by the *grating space* as measured by Davey, and tends to corroborate *Bohr's theory of atomic structure* according to which there is a discontinuity in atomic formation at argon, additional electrons going into inner shells.

Interatomic forces in cubic crystals.—*The crystal potential energy as a function of volume, at absolute zero* is determined from the experimental results, and an empirical expression for it is developed which is extrapolated to a volume so large that the repulsive forces between the atoms are small. The remaining attractive force is found approximately equal to that given by the expression derived by Madelung assuming each ion is singly charged. Then assuming electrostatic cohesion, a series development is obtained for the repulsion betwe atoms. This is found not to vary as any single inverse power of the grating space, as demanded by the theory of Born for salts of Na, K and Rb; nor is there any discontinuity between Li and the other metals. Values for the *energy of dissociation of the crystal* into ions are given. As would be expected, the change of compressibility with temperature is related to the thermal expansion in such a way that an increase of temperature and decrease of pressure have the same effect on both volume and compressibility.

I. INTRODUCTION

FOR some time physicists have been familiar with the idea that a crystal of a polar compound, such as sodium chloride, is simply a great molecule, its constituents being ions of sodium and chlorine. In such a substance, the forces between the ions have at the same time the character of chemical forces, cohesive forces, and the forces which resist compression; and the study of the forces in one of these roles immediately throws light on the forces in the others. Since the ions are supposed to be electrically charged, the metals positively, the halogens negatively, they necessarily attract each other; and it naturally has often been suggested, for example by Langmuir, that this attraction actually is the cohesive,

or chemical, force, and that when it has pulled the ions together until they bump, so that the crystal "molecule" is in equilibrium, the substance is in its normal state.

This idea has been developed into a quantitative theory by several German physicists: Born,[1] Lande, Fajans, Herzfeld, and others. They all agree in assuming the cohesive forces to be the electrostatic attraction of the ions for each other, and Madelung[2] has found from potential theory what the value of the attraction, or rather the potential energy associated with it, actually is for various crystal lattices. The differences between the developments of the various men lie only in their treatment of what has been roughly termed the "bumping" of the ions, the repulsion which they exert on each other when they come very close together, and which increases very rapidly as the distance between ions decreases. Born assumes that two ions, apart from their electrostatic action, repel each other with forces varying as the inverse tenth power of the distance, unless they are lithium ions, when they repel according to the inverse sixth power; the others have more elaborate developments in inverse power series, leading to somewhat different numerical results. These values for the repulsion rest on assumptions that the ions act like cubes of eight static electrons, with a nucleus in the center; the special value for lithium arises because lithium, with its two electrons, can hardly have cubic symmetry. Although I shall not discuss it in this paper, it seems to me that the argument on which these values rest, carried over of course to a dynamic atomic model such as those which Bohr has recently suggested, strikes certain difficulties in the way of stability, which make the whole picture of the mechanism of the repulsion of doubtful truth. In any case, the theory of the repulsion has a far less certain basis than that of the cohesive electric attraction.

The sum of the attractive cohesive force, and the "bumping" repulsion, is zero in the normal state at absolute zero of temperature; if it is not zero, it must stand in equilibrium with an external pressure or tension. It is thus plain that the vehicle for studying these chemical, or cohesive, forces is the compressibility. The first numerical check which Born made on his theory was on the compressibility of the salts for which that constant had been measured. Of the simple cubic alkali halides, the simplest set of polar compounds, six had been done, by Richards and Jones:[3] NaCl,

[1] Born and Lande, Sitzber. d. Preuss. Akad. d. Wiss. p. 1048, 1918; Verh. d. D. Phys. Ges. **19,** 210, 1918; Born, Verh. d. D. Phys. Ges. **21,** 13, 533, etc., 1919; Fajans, Verh. d. D. Phys. Ges. **21,** 539, etc., 1919; Fajans and Herzfeld, Zeits. f. Phys., **2,** 309, 1920; Schwendenwein, Zeits, f. Phys., **4,** 73, 1921.

[2] Madelung, Phys. Zeits. **19,** 529, 1918

[3] Richards and Jones, J. Am. Chem. Soc. **31,** 158, 1909

NaBr, NaI, KCl, KBr, KI. Born found fair agreement with his theory; the others also secured approximate agreement, but by no means exact. It seems likely from an examination of their results that the error lay in their values for the repulsion, in which they disagreed, rather than in the electrostatic attraction, which has a good theoretical foundation.

Bridgman[4] has very recently developed a new and much improved experimental method for measuring compressibility; and it is the purpose of this paper to state the results of an experimental investigation, by this method, on twice as many of the alkali halides as had been previously measured, and to see how much information these data are capable of yielding about the forces in the crystal. I wish to take this occasion to state my great indebtedness to Professor Bridgman for his constant interest and assistance during the research.

In previous theoretical work, it has been necessary to take the electrostatic nature of the cohesion for granted, and to assume that the approximate correctness of the results justified this. But the new measurements include not only the initial compressibility, but its initial change with pressure, which can be measured by use of a large pressure range (12,000 atmospheres). This gives a new term in the power series development of the potential energy of the crystal, and, by increasing the range of convergence, makes it possible to extrapolate to a negative pressure large enough so that the ions are theoretically pulled nearly out of contact, and the "bumping" repulsion has sunk to a low value, leaving principally the cohesive force by itself. This situation can naturally be more nearly reached with the soft salts, in which the ions touch loosely in the normal state, than in the hard ones. If now the cohesive force at the limit of extrapolation is compared with that to be expected on the electrostatic theory, it will be shown that the observed force approaches more nearly the theoretical as we pass to softer salts, departs from the theoretical in the direction to be expected on account of the remaining trace of repulsion, and approaches asymptotically almost exactly the correct value. This is as direct evidence for the electrostatic nature of the cohesion as could be desired.

If the electrostatic cohesion is regarded as established, then, since its theoretical value is known exactly, it is possible to put it on the known side of our equations, and concentrate the data on giving information about the other part of the force, the repulsive "bumping". First it is possible to see how far the theoretical assumptions of Born about this force are justified; in fact, we can set up for each salt, from experiment,

[4] Bridgman, Proc. Am. Acad., Jan., 1923

a fairly complete substitute for the function which Born assumed to be the inverse tenth power. But more important, we have here information about a series of ions, unaffected by chemical combination, and we can study the properties as we pass from one alkali to another, or one halogen to another. Actually, it is simpler not to try to eliminate the cohesive forces, but to consider periodic relations simply in the observed quantities. The number of salts studied is here, in contrast to previous work, large enough so that important information of this kind can be obtained, and the properties will be shown to have interesting connection with Bohr's recent theory of the periodic table.

II. Experimental Results

The experimental methods will be described in another place.[5] The measurement was performed by the new method used by Bridgman[4] in his recent work on the compressibility of metals. The samples were single crystals of the salts, artificially prepared in a new way by crystallization from the melted salt. Measurements of change of volume were made every thousand atmospheres up to 12,000 atmospheres, and at two temperatures, 30°C and 75°C. The change of volume is, within the limits of error of the experiment, a quadratic function of the pressure, so that the behavior at a single temperature can be described by two constants. If v is the volume of a certain quantity of substance, v_0 its volume under zero pressure, then the compressibility is defined as

$$\kappa = \frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_T. \tag{1}$$

If κ_0 is the value of the compressibility under zero pressure, then the change of compressibility with pressure may be conveniently defined as

$$\psi_0 = \frac{1}{\kappa_0}\left(\frac{\partial \kappa}{\partial p}\right)_T = \frac{1}{\kappa_0 v_0}\left(\frac{d^2 v}{dp^2}\right)_T. \tag{2}$$

The two constants ψ_0 and κ_0, for a fixed temperature, together with the change of compressibility with temperature $(1/\kappa_0)(\partial\kappa/\partial\tau)_p$, are the quantities measured. The change of compressibility with pressure was found to be independent of temperature.

The values of compressibility are probably correct to one per cent, except for one or two of the most incompressible salts; the error in the change of compressibility with pressure in most cases is probably between two and five per cent, in a few cases more. The change of compressibility with temperature is much less accurate; errors of ten or even twenty per cent are not impossible.

[5] Slater; paper will probably appear in Proc. Am. Acad.

In Table I data are given for the eleven salts which I have measured. Of these, the lithium and rubidium salts and KF have not been previously measured, although measurements on some of them, as yet unpublished, have recently been made at low pressures in Professor Richards's laboratory. NaI is the only salt previously done which I have not measured. RbBr and RbI were found to have polymorphic transitions at high pressures, presumably changing to a body centered form similar to the caesium salts. The data given are for the low pressure, simple cubic modifications. The quantities tabulated in Table I are the compressibility at 30°C, the change of compressibility with pressure independent of temperature between 30°C and 75°C, and the average change of compressibility with temperature between 30°C and 75°C. The compressibility and change of compressibility with pressure both have the dimensions of the reciprocal of a pressure; they are expressed in reciprocal dynes per square centimeter. The change of compressibility with temperature is in reciprocal degrees centigrade.

TABLE I

Compressibility, and its change with pressure and temperature, at 30° C

Salt	$-\kappa_0$	$-\psi_0$	$(1/\kappa_0)(\partial\kappa/\partial T)_p$
LiF	$1.53(10)^{-12}$	$11.7(10)^{-12}$	$1.9(10)^{-4}$
LiCl	3.41	19.8	6.9
LiBr	4.31	24.5	8.4
NaCl	4.20	21.9	6.8
NaBr	5.08	25.5	7.5
KF	3.31	20.1	1.2
KCl	5.63	26.5	4.8
KBr	6.70	31.8	6.0
KI	8.54	39.1	6.0
RbBr	7.94	35	
RbI	9.58	43.0	6.8

For purposes of comparing various salts, these data, for 30°C, are satisfactory; but for theoretical use, when the temperature effects are to be neglected, the value of the compressibility for the absolute zero should be employed. The change of compressibility with temperature provides a means of approximately reducing the compressibilities to the absolute zero, if it is assumed that the change of compressibility with temperature is independent of temperature. This is probably not true; it seems likely for theoretical reasons that the change of compressibility with temperature should become small at very low temperatures. But the compressibility at absolute zero found in this way is certainly nearer the truth than the observed value at room temperature, which has been used for all previous theoretical work.

In Table II are given the compressibilities of the salts at absolute zero found by extrapolation. There are also given two quantities of theoretical interest, in which δ_0 is the grating space at no pressure (the distance between successive ions of the same sign, measured by Davey),[6] corrected to the absolute zero by assumed values of the thermal expansion, in cases where this has not been measured. The significance of these quantities will be explained later.

TABLE II

Compressibility and derived quantities at absolute zero.

Salt	$-\kappa_0$	$(1-9\delta_0^4/13.94e^2\kappa_0)$	$(3\psi_0/\kappa_0-10)$
LiF	1.4×10^{-12}	5.9	14.3
LiCl	2.7	8.0	11.9
LiBr	3.2	8.7	12.8
NaCl	3.3	9.1	9.8
NaBr	3.9	9.5	9.5
KF	3.2	7.9	8.9
KCl	4.8	9.7	6.5
KBr	5.5	10.0	7.1
KI	7.0	10.5	6.8
RbBr	6.5	10.0	6.2
RbI	7.6	11.0	6.8

III. SERIES DEVELOPMENT FOR CRYSTAL ENERGY

Before making numerical use of the data, it is necessary to derive the formulas for finding as much as possible about the energy of the crystal from the compressibility and its change with pressure. This discussion will refer to the absolute zero of temperature, so that, disregarding the electronic motions, the energy will be wholly potential.

Since no heat is to be absorbed in compression at the absolute zero, the first law states that $0=d\varphi+pdv$, where p is the pressure, and φ is the potential energy in a cube of volume v whose side is the grating space δ, now regarded as a variable. That is,

$$p=-d\varphi/dv. \tag{3}$$

It is desired to write κ and ψ, defined in Eqs. (1) and (2), in terms of derivatives of φ with respect to δ, instead of in terms of derivatives of v with respect to p, so that by inversion the derivatives of φ at zero pressure can be found in terms of κ_0 and ψ_0. This will be done in two steps. First, the derivatives of v with respect to p will be written in terms of derivatives of φ with respect to v; then these will be changed to derivatives with respect to δ.

[6] Davey, Phys. Rev. **21**, 143, 1923.

We have, from (3),

$$\frac{dp}{dv}=-\frac{d^2\varphi}{dv^2}, \quad \frac{dv}{dp}=-1\Big/\frac{d^2\varphi}{dv^2}.$$

Then $$\frac{d^2v}{dp^2}=\frac{dv}{dp}\frac{d}{dv}\left(\frac{dv}{dp}\right)=-\frac{d^3\varphi}{dv^3}\Big/\left(\frac{d^2\varphi}{dv^2}\right)^3=\frac{d^3\varphi}{dv^3}\left(\frac{dv}{dp}\right)^3.$$

Next let $v=\delta^3$, $d\delta/dv=1/3\delta^2$. Denoting derivatives of φ with respect to δ by primes,

$$\frac{d\varphi}{dv}=\frac{d\varphi}{d\delta}\frac{d\delta}{dv}=\frac{\varphi'}{3\delta^2}; \quad \frac{d^2\varphi}{dv^2}=\frac{d}{d\delta}\left(\frac{d\varphi}{dv}\right)\frac{d\delta}{dv}=\frac{\varphi''}{9\delta^4}-\frac{2\varphi'}{9\delta^5};$$

$$\frac{d^3\varphi}{dv^3}=\frac{d}{d\delta}\left(\frac{d^2\varphi}{dv^2}\right)\frac{d\delta}{dv}=\frac{\varphi'''}{27\delta^6}-\frac{2\varphi''}{9\delta^7}+\frac{10\varphi'}{27\delta^8}.$$

We are interested in quantities at zero pressure. Denoting these by zeros, we have, from (3), $(d\varphi/dv_0)=0$. Then $\varphi'_0=0$, and

$$\left(\frac{d^2\varphi}{dv^2}\right)_0=-\frac{\varphi_0''}{9\delta_0{}^4}; \quad \left(\frac{d^3\varphi}{dv^3}\right)_0=\frac{\varphi_0'''}{27\delta_0{}^6}-\frac{2\varphi_0''}{9\delta_0{}^7}=\frac{\varphi_0'''}{27\delta_0{}^6}-\frac{2}{\delta_0{}^3}\left(\frac{d^2\varphi}{dv^2}\right)_0.$$

Substituting these in the derivatives of v with respect to p, and these in (1) and (2), we have

$$\kappa_0=-9\delta_0/\varphi_0''; \quad \psi_0=\kappa_0{}^2\varphi_0'''/27+2\kappa_0. \tag{4}$$

These can now be solved for the derivatives, giving

$$\varphi_0'=0; \quad \varphi_0''=-9\delta_0/\kappa_0; \quad \varphi_0'''=(27/\kappa_0)/(\psi_0/\kappa_0-2). \tag{5}$$

Eq. (5) gives all the information about the energy which can be gained from these experiments. From them a Taylor's expansion can be immediately written down. Using $d=\delta/\delta_0$ as a variable, it is

$$\varphi=\varphi_0-\frac{9}{2}\frac{\delta_0{}^3}{\kappa_0}\left\{(d-1)^2-\left(\frac{\psi_0}{\kappa_0}-2\right)(d-1)^3+\ \ldots\ \right\}. \tag{6}$$

Eq. (6) is an empirical expression for the potential energy, and may be expected to represent the function only for values of d near enough to unity so that the remaining terms are small. To proceed further, it is desirable to inquire what the main features of the function may be expected to be.

The energy will show a minimum at the position of equilibrium, rising on each side. For values of d less than unity, there is no reason to suppose that the energy will not rise indefinitely, so that an indefinitely large amount of work can be done before reducing the volume of the crystal to zero. But for values of d greater than unity, the rise cannot be indefinitely large as it requires only a finite amount of work to pull the crystal apart so that its ions are a large distance from each other. Thus the curve may be expected to rise with increasing d, and approach

a horizontal asymptote. This part of the curve, where the force is attractive, will be much less steep than the other part, where it is repulsive. The energy will naturally be divided into parts: the slowly changing attractive energy, presumably electrostatic, and the repulsive energy, which is small at large distances, but becomes rapidly large near the position of equilibrium.

IV. The Cohesive Attraction

We shall first seek information about the attractive energy. The method of doing this has already been described. We shall find the empirical value of the force, or of φ', for as large a value of d as we can; and we shall compare this with the theoretical value of φ'. The extrapolated value of φ' will first be found. To do this, we must consider more closely the nature of the empirical series. There are two terms. The first is a quadratic, a parabola rising indefinitely for values of d both less than and greater than $d=1$. The two terms together form a cubic, rising higher than the parabola for d less than 1, but for greater values rising first, although not so high as the parabola, but passing through a point of inflection, a maximum, and finally falling. It seems most likely that all the higher terms for $d<1$ will have the same sign, so that for $d>1$ the series will be alternating. If the terms decrease regularly, the final value of the series will not be far from half way between the first and second approximation; it will certainly lie somewhere between them, and the mean will furnish a good approximation. It is hardly possible to use the series for values of d greater than that for which the cubic has its point of inflection. This value of d increases as the compressibility of the salt increases, from 1.055 for LiF to 1.093 for RbI. But at the point of inflection, the mean of the slopes of the first and of the second approximations should form a good value of φ'. This value may be compared with the value of φ' to be expected on the electrostatic hypothesis, and the value of the charge necessary to produce the observed φ' may be found. This charge may be expected for the incompressible salts to be considerably smaller than the charge actually present, since d for these salts is small and at the same time the ions are tightly packed together and they would have to be separated by a considerable distance before the repulsion vanished; for the compressible salts, on the other hand, the computed charge should be much nearer the actual charge. If the charge is the same for all the salts, and if the computed charge is plotted against compressibility, the curve should approach an asymptote for large values of compressibility, this asymptote representing the actual charge on each ion; if on the other hand the computed charge is plotted against the

reciprocal of the compressibility, and the curve extrapolated to zero, the intercept should be the actual charge. This will now be done.

At the point of inflection of (6), $\varphi''=0$, or $2-6(\psi_0/\kappa_0-2)(d-1)=0$, $d=1+1/[3(\psi_0/\kappa_0-2)]$. At this point, the first term of φ' is $-3\delta_0^2/[\kappa_0(\psi_0/\kappa_0-2)]$ and the first two together $-3\delta_0^2/[2\kappa_0(\psi_0/\kappa_0-2)]$; the mean is $-9\delta_0^2/[4\kappa_0(\psi_0/\kappa_0-2)]$. The theoretical value of φ', as mentioned above, is a constant divided by δ^2; this constant has been computed from potential theory by Madelung,[2] who finds the value of φ' for a simple cubic lattice to be $13.94e^2/\delta^2$, where e is the charge on each ion. Setting this equal to the other expression for φ' gives

$$e=\tfrac{3}{2}\,\frac{\delta_0^2}{\sqrt{[-13.94\ (\psi_0-2\kappa_0)]}}\left\{1+\frac{1}{3(\psi_0/\kappa_0-2)}\right\}.$$

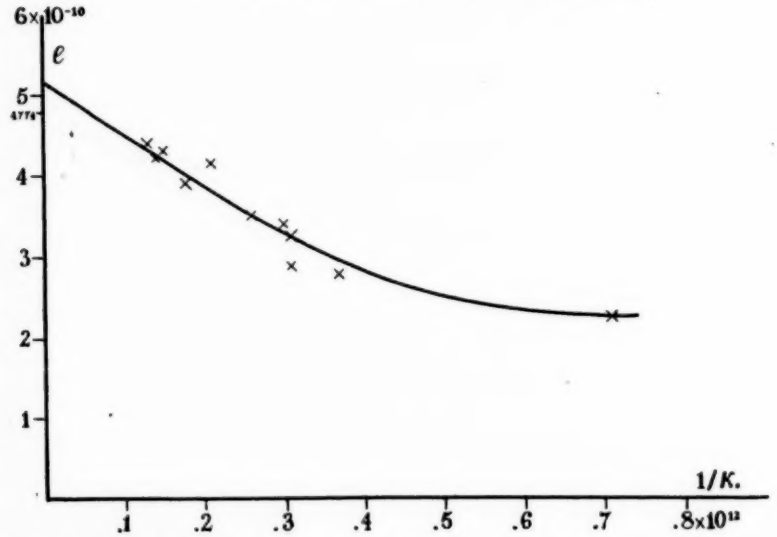

Fig. 1. Computed charge on ions, plotted against reciprocal of compressibility.

In Fig. 1, these values of e for the various salts are plotted against the reciprocals of the compressibility. The behavior of the curves is similar to what was expected. But more than that, the extrapolated value of e is 5.1×10^{-10} e.s.u., very close to the charge on the electron, showing that, if the attraction actually is electrostatic, the charge on each ion is one electronic charge. This seems to be very convincing evidence for the electrostatic nature of the cohesive forces.

V. The Atom Repulsion

Once the hypothesis is accepted that the source of the attractive force is electrostatic, the exact expression for this part of the energy becomes known, and by subtraction the Taylor's development of the repulsive

part of the energy can be found. This energy will be expected to sink to zero for values of d not far greater than unity; and the condition of approaching an asymptote, together with the requirement that the curve lie between the two approximation curves, is enough to fix the course of the function fairly completely. The region in which there is uncertainty, between the point where the second approximation ceases to represent the function and the point where the function is very small, is not large. By a simple method of interpolation, which need not be described here, it has been possible to fill in the intermediate part, thus affording a complete knowledge of the repulsive energy, and, by addition, of the total energy. One result of this is a knowledge of the magnitude of the energy of the crystal in the normal state. If the energy for infinitely large δ is taken to be zero, then the energy in the normal state is the sum of the negative energy of the attractive term, found simply from the grating space, and of the positive repulsive energy, determined from the empirical curves, and depending to some extent on the interpolation used in completing the curve. This last part of the energy amounts to about ten per cent of the whole. In Table III are the negative energies of the crystals in the normal state, calculated in the manner sketched. The

TABLE III

Lattice energies, from compressibility data, in kg-cal/g-mol

	Li	Na	K	Rb
F	231		182	
Cl	189	178	164	
Br	180	169	157	152
I			148	147

values are for absolute zero of temperature, and are naturally derived directly from the compressibility. The data are given in kg-cal/g-mol, for convenience in thermochemical applications. For the salts other than KF and those of Li, the figures are probably not in error by more than five kg cal. They differ by less than this in many cases from the values calculated by Born from his theory, which will be described next.

Born's formula for the energy, as indicated above is

$$\varphi = -13.94\ e^2/\delta + b/\delta^n \qquad (7)$$

where the first term is the electrostatic potential already considered, and the second is a hypothetical representation of the repulsive potential. The value of n is 9 for salts other than those of lithium, and 5 for those of lithium. It is well to see how nearly the data fit such a law.

The comparison could, of course, be made between the curves which can be drawn for the repulsive energy from experiment, and the inverse power law; but it is easier to make a more direct check. We can differ-

entiate (7), and substitute in (4), eliminating b by (5), and obtaining directly

$$\kappa_0 = -9\delta_0^4/(n-1)\ 13.94\ e^2; \quad \psi_0 = \kappa_0(n+10)/3.$$

These can be put in the form

$$n = 1 - 9\delta_0^4/13.94\ e^2\kappa_0 = 3\psi_0/\kappa_0 - 10. \tag{8}$$

Eq. (8) states a condition that must be satisfied by the experimental quantities if the repulsive energy is to be represented by a single inverse power term. The two quantities of (8) are given in Table II; and it is seen that, while they are of the same order of magnitude, they are by no means equal; the first shows a regular increase passing down the list, the second a regular decrease. Thus Born's assumption is not justified; even more, the assumption that $n=9$ for all salts except those of lithium, 5 for those of lithium, is incorrect. There is no discontinuity between the properties of lithium and of the other metals.

VI. Relations in the Periodic Table

We have considered the character of the repulsive action for the separate salts; but more information about the ions can be obtained by treating them in the series to which they belong in the periodic table. The alkali halides form a very simple two parameter family of compounds, especially suited for investigating the comparative properties of the ions. For salts of a given halogen, there should be a regular progression of properties passing along from the lithium, sodium, potassium, to rubidium salts. Similarly, there should be a regular progression from the fluoride to the chloride, bromide, and iodide of the same metal. It is interesting to plot not only the compressibility and its change with pressure, but also the grating space, in this way, against both alkalis and halogens. This is done in Fig. 2, where the abscissas represent the rare gas configurations which the corresponding ions resemble, equally spaced. The quantities plotted are the data for 30°, since these are more accurate than at the absolute zero. All these quantities increase as either of the ions increases in size. The interpretation of this is that as electrons are added to either kind of ion, the ions grow larger, the forces between them become less, they are less squeezed together initially, and a given external pressure has more effect in compressing them. But, in addition to this, and to the obvious regularity of the curves, it is seen that the curves plotted against the metals all show a break at potassium, and against the halogens at chlorine. These both correspond to the argon shell; and the fact that every one of the curves shows this behavior is convincing demonstration that there is some discontinuity at argon in the formation of the series

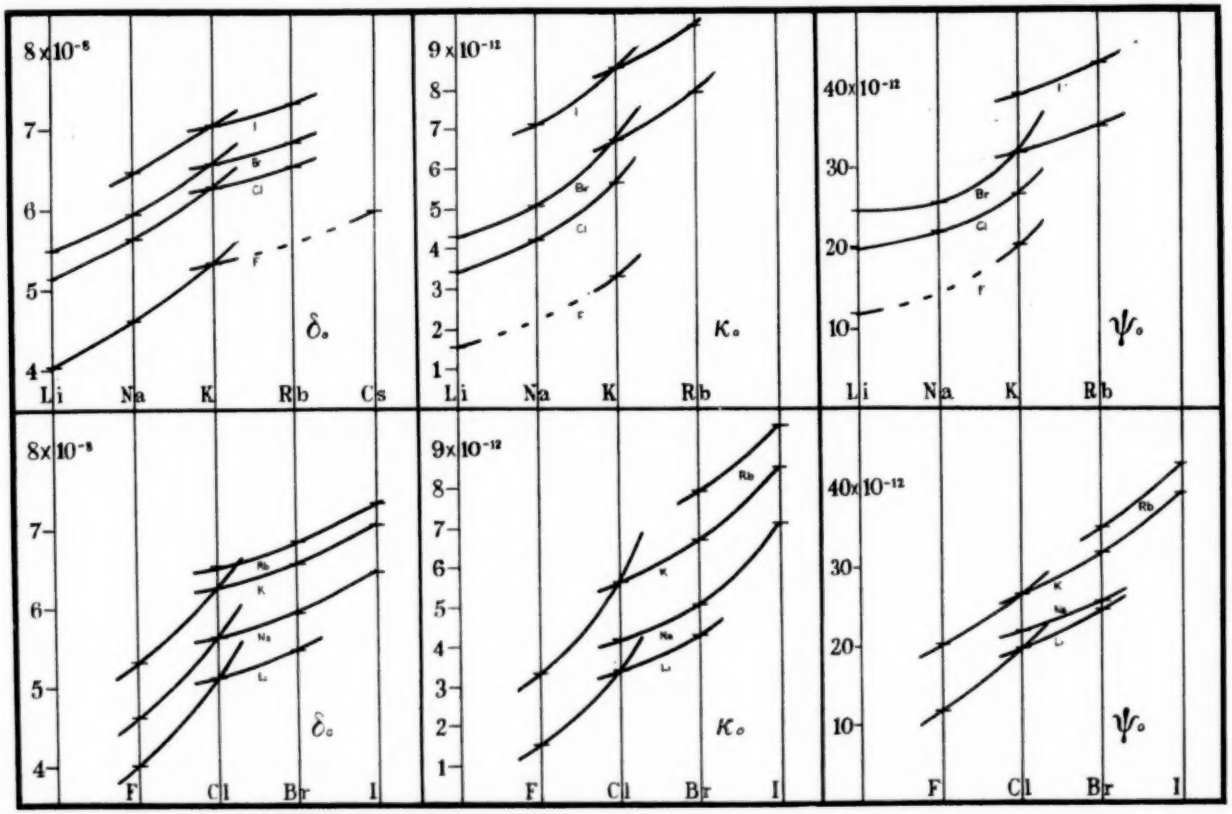

Fig. 2. Grating space, compressibility, and change of compressibility with pressure, at 30°C, plotted against metals and halogens.

of inert gases, and that it is really a property of the ion, not of the salts. The electrons added after argon have less effect on the external properties of the atom than those added before. But this is exactly in accord with Bohr's recent views of the relation between electron structure and the periodic table; at argon, the electrons added as the atomic weight increases stop going into the outer shell, but fill out the inner shell instead. Thus a discontinuity at this point would be strongly indicated theoretically.

VII. Temperature Effects

The discussion so far given refers merely to the absolute zero. No attempt at discussing the temperature effects will be given here. But almost any theory would demand that the effect of an increase of temperature on all the properties should be equivalent to a certain decrease of pressure, that is, that the change of compressibility with temperature should be to the change of volume with temperature (the thermal expansion) as the change of compressibility with pressure is to the change of volume with pressure (the compressibility). The thermal expansion has been measured, as far as I can find, for only four of the salts; but for these, this relation is found to be approximately fulfilled. This insures that any theory capable of describing the thermal expansion will at the same time give correctly the change of compressibility with temperature.

Jefferson Physical Laboratory,
Harvard University,
July 21, 1923.

THE MODIFICATION OF THE THERMIONIC CURRENT IN VACUUM TUBES WHEN POTASSIUM DEPOSITED ON THE INSIDE WALLS OR GRID OF THE TUBE IS ILLUMINATED

By J. M. Hyatt

Abstract

When a floating grid mounted between a plate and filament in a spherical tube, is coated with potassium and illuminated, it loses a negative charge and produces a considerable increase in the plate current, equivalent to that due to maintaining the unilluminated grid at a positive potential of a few volts relative to the filament. In the case of a long tube with a constricted cylindrical portion between the plate and filament ends, an illuminated coating of potassium on the walls reduces the tendency of the walls to charge negatively and hence facilitates the passage of the current through the tube. As the filament current is increased for a given plate voltage the current reaches a maximum, then suddenly drops to a minimum, due to the combined action of space charge and photo-electric emission.

Introduction

THE discovery by Case[1] of the increased thermionic current from the filament in an audion bulb when it was illuminated, led to investigation of the action of light on vacuum tubes by Merritt,[2] Miss Meacham,[3] Gibbs,[4] Arnold and Ives.[5] Later Case constructed a vacuum tube with a deposit of potassium on the plate and walls of the tube. This tube behaved in a characteristic manner when the intensity of illumination on the potassium was varied. There was a diminution in the plate current as the illumination was reduced, which was suspected to be due to the patches of potassium on the walls charging up negatively as electrons were received by the surface. When the illumination was increased, the increase in the plate current was probably due to the loss of photo-electrons from the potassium, causing its potential to become more positive. Thus the insulated patches of potassium appeared to serve as a grid in a three electrode tube.

The following experiments were made to test this view.

[1] Case, Phys. Rev. **17**, 398 (1921)
[2] Merritt, Phys. Rev. **17**, 525 (1921)
[3] Miss E. L. Meacham, Master's thesis, Cornell University, Sept. 1921
[4] R. C. Gibbs and Miss Meacham, Phys. Rev. **19**, 415 (1922)
[5] Arnold and Ives, Proc. Nat. Acad. Sci., **7**, 323 (1921)

Method of Experiment

The grid of the tube shown in Fig. 1 was coated with potassium by evaporating a piece of potassium while the other parts of the tube were heated. This tube was used in the ordinary circuit for determining the characteristic curves of vacuum tubes, the current measuring instrument being a galvanometer of about 9,000 megohms sensitivity.

The first test, which was made with the grid floating and unilluminated, showed that the plate current was too small to measure until the filament plate potential was increased to 50 volts. The plate current, with the grid illuminated by a 100-watt lamp at a distance of 150 cm, however, had reached a value within a few per cent of saturation at 20 volts. These facts are shown by curves F and E in Fig. 2. The other curves in Fig. 2 show the relations between the plate current and filament-plate potential while the grid was maintained at definite potentials with respect to the filament.

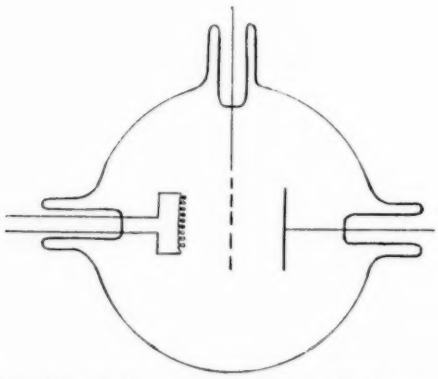

Fig. 1. Diameter of tube 11 cm; filament and plate 4 cm apart.

These curves show that an increase in the potential of the grid when dark gives rise to an increase in the plate current. Since this is true and since the illumination of the floating grid causes a corresponding increase in the plate current, the effect of the illuminated grid must be equivalent to maintaining the grid at a small positive potential relative to the filament. This must be accomplished by the discharge of the photo-electrons from the grid when illuminated. Further experimenting showed that the increase in plate current became almost zero when the grid was illuminated if it was maintained at a potential of 4 volts or above with respect to the filament.

When the intensity of illumination on the floating grid was varied, it was found that there was a linear relation between the plate current and light intensity. Since the effect of changing the intensity of illumination

on the potassium-coated grid is to change its potential over a small range, the above linear relation must correspond to a portion of the ordinary plate current-grid potential characteristic.

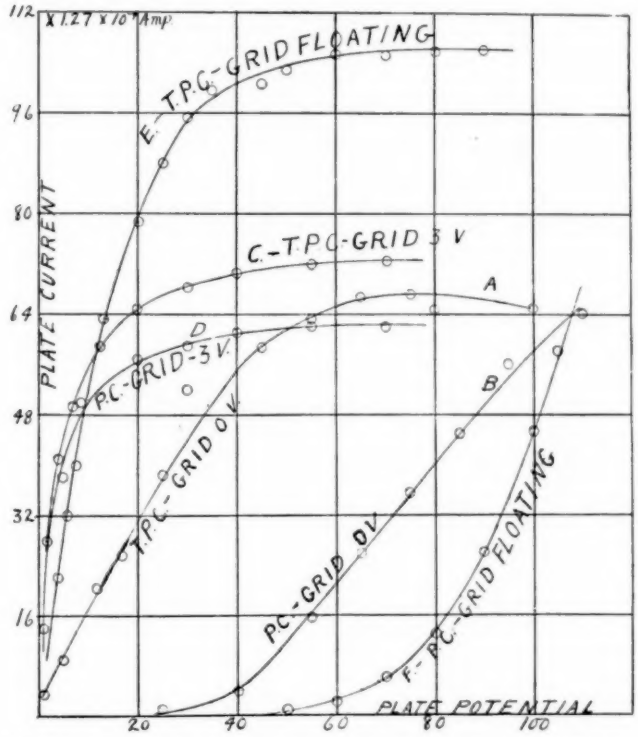

Fig. 2. T.P.C. means total plate current with grid illuminated; P.C. means plate current with grid unilluminated.

It seemed worth while to investigate the effect on the plate current due to a change in the distribution of the potassium between the filament and plate. As a means of studying this question the tube shown in Fig. 3 was made. The inside of the constricted portion of the tube was coated

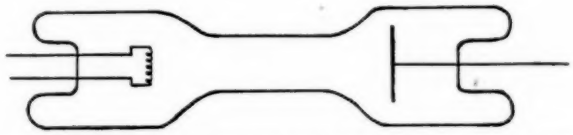

Fig. 3. Length of tube 16 cm; filament and plate 7.5 cm apart; diameter of constricted portion of tube 1.5 cm.

with potassium except for a narrow window through which it could be illuminated. The curves in Fig. 4 show for different filament-plate potentials the relation between the photo-electric current and the filament

current when the whole tube was illuminated. There was no current in the dark until a potential of about 260 volts was applied. This was undoubtedly due to the retarding action of the negatively charged walls of the tube.

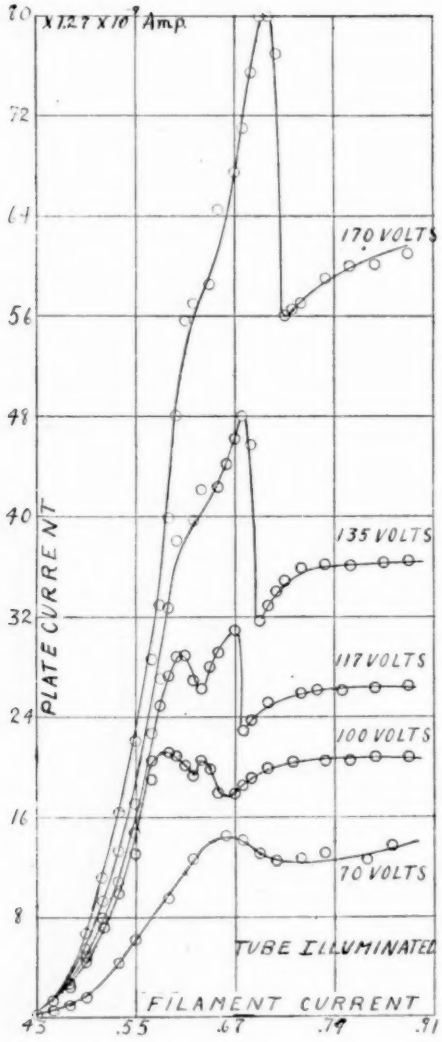

Fig. 4

The outstanding peculiarity about these curves is the sudden drop in the plate current at certain filament currents. The higher the filament plate potential, the higher is the filament temperature at which these drops occur. The observations were repeated twice on different days and the characteristics of the above curves were duplicated except for a

small percentage variation in the magnitude of the photo-electric currents. Observations that were taken for successively decreasing filament currents checked those for increasing currents to within a very few per cent.

When the whole tube was illuminated, the greater the light intensity, the hotter the filament had to be for a given plate potential for the drop in the photo-electric current to take place. When a narrow beam of light was thrown on the tube at different distances from the filament, it was found that the farther the illuminated area was from the filament, the hotter the filament had to be before the drop in the plate current occurred.

With these results in mind, the plate potential and filament current were set to give the lowest point on one of the curves in Fig. 4 after the drop in the photo-electric current. A screen was then lowered from the filament end of the tube covering up a portion of the illuminated potassium. The photo-electric current then increased a little and continued to increase as the tube was covered up until the current reached its value before falling; then the current decreased as more of the tube was covered. When the screen was raised to the position giving the maximum current and the filament temperature increased a little, the photo-electric current then fell to a smaller value but came back up when a little more of the tube was covered. This was repeated several times until a little more than half of the potassium was in the dark, after which the current decreased no matter what the filament current. This experiment was repeated several times with the same result.

The following considerations may explain the peculiarity in the curves. An increase in the filament temperature means an increase in the space charge or electron density near the filament. As the supply of electrons increases, the current through the tube increases until the electron density reaches a certain value. Further increase in this density hinders the light from discharging the photo-electrons from the potassium on account of the mutual repulsion of the electrons, the potential of the potassium decreases and hence the current, as is observed. If now the potassium in this region is covered its potential is still low and a potential gradient is established between the dark potassium surface and the illuminated portion near the plate. The electrons now are conducted over the potassium surface until they reach the illuminated portion where they are emitted and travel to the plate under the action of the field, thus bringing the current through the tube to its original value.

To test this explanation, the potassium was driven from a narrow ring around the tube about halfway between the filament and plate by heating that part of the tube. The photo-electric filament current character-

istics of the tube under these conditions were similar to those shown in Fig. 4. There were no indications of an increase in the current as part of the tube was covered, but a considerable portion of the potassium could be covered with but a small decrease in the current. This was to be expected if the presence of the ring prevented conduction along the surface. While attempting to redistribute the potassium again the tube was broken, and so further investigations to test the theory of the action of the potassium have not been made.

The writer extends to Mr. T. W. Case his appreciation and thanks for the manufacture of the tubes that were used in the investigation. He also wishes to express his gratitude to Professor Gibbs, under whose direction this investigation was made, for his advice and encouragement throughout the work, and to thank Professor Merritt for his suggestions and interest in this problem.

CORNELL UNIVERSITY,
August 3, 1923.

THE POWER LOSS IN CONDENSERS WITH LIQUID DIELECTRICS

By Louise S. McDowell

Abstract

Power loss in condensers with liquid dielectrics; variation of equivalent series resistance and capacity with frequency, 600 to 3500 cycles.—Using a variable test condenser with conical plates nickel plated, measurements for frequencies below 3700 were made with a special capacity bridge previously described by MacLeod, and for higher frequencies to 1,500,000 cycles by an ordinary resonance substitution method. *Castor oil, benzene, xylene, toluene, olive oil, paraffine oil, medicinal oil, "Bostonia," glycerine and oil of turpentine* were studied; results are given for the first five. The power loss per unit voltage $R\omega^2C^2$ is approximately constant for benzene, xylene and toluene, decreasing only from 202 to 184, from 102 to 90 and from 138 to 117 (all times 10^{-10} watts), respectively, as the frequency increased from 700 to 3500. This indicates that the loss is due chiefly to conductivity, but in some liquids, notably xylene, there is apparently a small additional loss which decreases with the frequency but which does not fit the equation for dielectric absorption. Castor oil and olive oil show a loss per unit voltage increasing with frequency, suggesting two leaky condensers in series.

THE cause of the failure of liquids to act as perfect dielectrics has been studied by various investigators, who have generally agreed that the power loss in condensers with liquid dielectrics in alternating current circuits is due to conductivity alone. Tank[1] concludes from his experimental study that "In fluids one is without doubt dealing with genuine ionic conductivity. Whether this is a definite property of the substance appears questionable, since it depends strongly on accidental, often very slight impurities." He is inclined to regard the ideal pure liquid dielectric as a perfect non-conductor. Tank's work confirms the conclusions of von Schweidler,[2] based on both theoretical and experimental considerations.

In the work of earlier investigators one of two methods was usually employed: (1) the direct measurement by a dynamometer or watt-meter of the power loss in a condenser in an alternating current circuit, and its comparison with the loss calculated from the measurement of the direct current conductivity,[1] or (2) the measurement at some one, or at most two or three frequencies, of either the parallel or equivalent series resistance of the condenser.[3] In the present investigation the method

[1] Franz Tank, Ann. der Phys. **48**, 307, 1915
[2] E. R. von Schweidler, Ann. der Phys. **24**, 711, 1907
[3] Hanauer, Wied. Ann. **65**, 789, 1898

chosen was the study of the law of variation with the frequency of the alternating current, of the equivalent series resistance and capacity of a condenser with various liquid dielectrics.

Apparatus

For frequencies from 600 to 3700 cycles the measurements of capacity and resistance were made with a capacity bridge. For high frequencies a resonance substitution method was used. The writer was so fortunate as to have the use of a special capacity bridge designed in the Cruft Laboratory by H. J. MacLeod and used by him for a similar study of

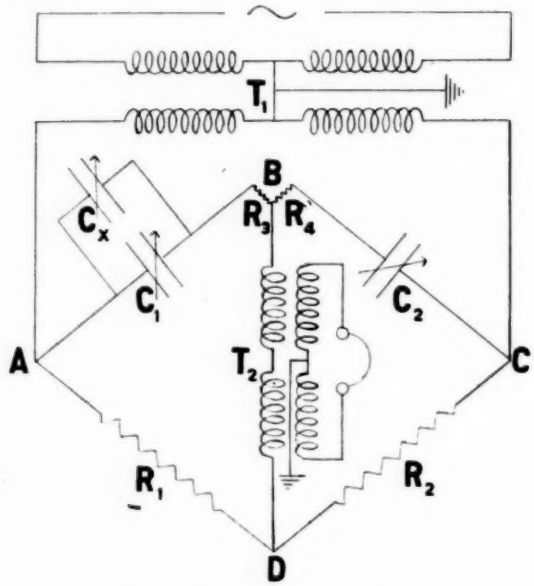

Fig. 1. Diagram of bridge circuit.

condensers with solid dielectrics. A full description of this bridge and the theory may be found in an article by MacLeod.[4] The diagram of the bridge circuit is shown in Fig. 1. One advantage in such a bridge is that the measurement of the resistance does not rest upon the assumption that the losses in a standard air condenser are negligible.

The bridge was excited by a vacuum tube oscillator with a Hartley circuit, placed in an adjoining room. To minimize errors in balance due to overtones, the secondary was rather loosely coupled to the primary and was tuned to the same frequency. From the condenser in the secondary circuit leads ran through a wall to the input transformer of the bridge about ten feet away. Resonance was found by a thermo-electric volt-

[4] MacLeod, Phys. Rev. **21**, 53, 1923

meter which served also to measure the potential difference applied to the bridge terminals, which ranged from 70 to 100 volts. The frequency was measured by a frequency-meter formed of a variable oil condenser in series with a large 6-step inductance. Resonance was indicated by a pair of telephones, of which only one terminal was connected to the condenser, the other terminal being grounded or held in the hand. This frequency-meter was calibrated by comparison both with the Cruft frequency-meter and with standard tuning-forks by the method of beats.

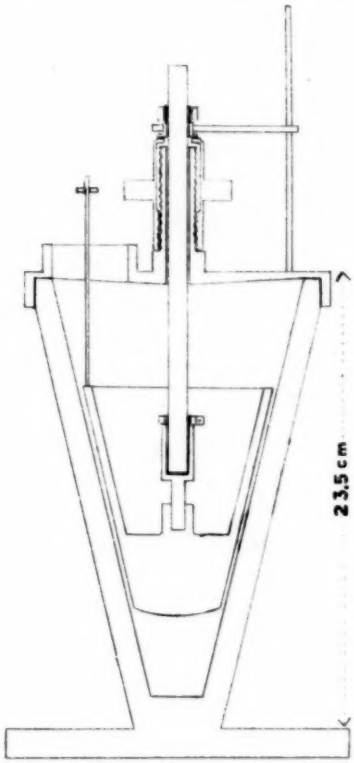

Fig. 2. Test condenser

The test condenser was conical in shape, heavily nickel plated, the inner cone supported by a single pyrex glass rod, accurately turned, the only dielectric used in the construction. The details are shown in Fig. 2. The rod was clamped at the bottom to the inside of the inner cone and at the top held by another clamp which rested on a large screw with knurled head, and was prevented from rotating by a guide rod. By raising or lowering the screw on the metal cover which formed part of the outer plate the distance between plates could be varied. The cones were centered with sufficient accuracy to permit adjustment of the minimum

distance between plates to about one-half a millimeter without danger of short circuiting. A hole in the cover four centimeters in diameter permitted filling and also the bringing out of the terminal from the inner cone. The cover was slightly conical to prevent trapping air.

The standard condenser was a General Radio Variable Precision Condenser, type 222, very accurately calibrated.

Procedure

The condenser was completely taken apart, washed in hot water and ivory soap until traces of oil no longer appeared, thoroughly rinsed several times in hot distilled water, reassembled, filled with the oil to be tested, and exhausted under a bell jar until the oil ceased to bubble. It was then left for a period, usually of at least twenty-four hours, in the constant temperature room before measurements were taken. The distance between cones was adjusted to make the capacity approximately 900$\mu\mu$f, and the capacity and series resistance measured for frequencies ranging from 600 to 3700.

To measure the capacity the test condenser C_x was placed in parallel with the capacity C_1 in one arm of the bridge, as shown in Fig. 1, the bridge balanced in the usual way, and readings taken of the value of R_4 holding R_3 constant. The test condenser was then replaced by the precision condenser, and the bridge again balanced. The capacity C_x was therefore obtained by direct substitution. For these readings the high potential plates of the condenser C_1 were removed to make the capacity as small as possible. To measure the equivalent series resistance the high potential plates of C_1 were replaced, the test condenser removed, the bridge again balanced keeping C_2 unchanged, and the readings of R_4 taken as before. Since the resistance of the high potential condenser plates added was negligible, the difference between the values of R_4 with and without the test condenser gave the equivalent series resistance R_s of the two condensers C_1 and C_x in parallel. Since C_1 was considered to be acting as a pure capacity, the equivalent series resistance of the test condenser R_x was obtained from the formula

$$R_x = R_s\,(C_x+C_1)^2/C_x^2$$

As the value of C_1 with high potential plates removed, as measured by MacLeod,[4] was only 32$\mu\mu$f, the factor $(C_x+C_1)^2/C_x^2$ ranged from 1.071 to 1.078 for the values of C_x used.

Test of Resistance Measurements

Although in the neighborhood of 1000 cycles a balance could often be obtained to the nearest tenth ohm, and usually at all frequencies above

that to within half an ohm, below 700 cycles it was difficult to balance the resistance within one ohm.

To test the accuracy of the measurement of the equivalent series resistance at different frequencies a sputtered resistance was placed in series with the precision condenser and the equivalent series resistance measured with and without this sputtered resistance in series. The mean deviation from the average value of 714.6 was only 0.3 ohm or 0.04 per cent which is well within the other experimental errors.

High Frequency Measurements

With one or two exceptions the decrease in resistance with increasing frequency was so rapid that it was unnecessary to make measurements at frequencies above 3700. When necessary a simple resonance substitution method was used. The secondary was very loosely coupled to the primary circuit. Resistance was introduced by a General Radio decade resistance box placed next the grounded end of the condenser. Resonance was indicated by a thermo-couple and sensitive galvanometer placed also on the low potential side. By means of a double-pole, double-throw switch the test condenser and the precision condenser could be alternately thrown into the circuit. The circuit was first adjusted to resonance and the galvanometer deflection read with the test condenser in the circuit; the precision condenser was then substituted and the capacity adjusted to produce resonance again. Resistance was next added to bring the deflection to the same value and if necessary for resonance the capacity was readjusted. This added resistance represented the difference between the equivalent series resistances of the test condenser and the precision condenser. Since the resistance of the precision condenser, as found by extrapolation from the curve obtained from the bridge measurements, was less than 0.2 ohm at a frequency of 30,000 cycles and diminished to 0.05 ohm at 60,000 cycles, it was considered negligible at frequencies above 50,000. The resistance measurements usually agreed with one another within a few tenths of an ohm and showed also remarkably good agreement with the measurements by the bridge method, as may be seen by reference to Fig. 6, Curve 2, where the first point ($R=9.8$ ohms) was obtained by the resonance method at a frequency of 33,000.

Discussion of Data

The dielectrics tested were: castor oil, 2 samples; paraffine oil, commercial; medicinal oil, "Bostonia," probably purified paraffine oil; olive oil; toluene; glycerine; zylene; benzene, c.p.; oil of turpentine (Merck) U. S. P. IX rectified.

Of the dielectrics studied the commercial paraffine oil was unsuited for exact measurements because of the presence of acid which acted on the nickel plating and produced an increasing leak. The purified oil "Bostonia" showed the smallest losses of any. The values of the series resistance were too small to be measured with accuracy, ranging from 2 to .2 ohm, for frequencies from 600 to 1300 cycles. So far as could be judged they indicated loss due to leakage only. The sample of glycerine on the contrary gave losses too large to be measured accurately with the resistances available. Toluene, benzene, zylene and oil of turpentine were similar in their behavior. Typical data for benzene are given in Table I. Castor oil and olive oil showed a decidedly different behavior. Typical data for castor oil are given in Table II.

TABLE I

Benzene, at temperature 18.7°C

f	R (ohms)	C (farads $\times 10^{-12}$)	$R\omega C$	$R\omega^2 C^2$ (watts $\times 10^{-10}$)
601	1726	909.0	.00592	203
637	1550	908.6	.00564	205
670	1392	908.7	.00532	204
722	1207	908.7	.00498	205
775	1041	908.8	.00461	204
888	772	908.7	.00391	198
968	633	908.7	.00350	193
1090	499	908.7	.00311	193
1282	356.5	908.8	.00261	191
1358	320.8	908.8	.00249	193
1658	217.6	908.7	.00206	195
1938	157.5	908.3	.00174	193
2228	116.5	908.7	.00148	189
2842	70.8	909.2	.00115	187
3253	53.7	908.6	.000997	185
3525	44.8	908.6	.000902	181

TABLE II

Castor Oil

f	R (ohms)	C (farads $\times 10^{-12}$)	$R\omega C$	$R\omega^2 C^2$ (watts $\times 10^{-10}$)
		Temperature 19.8°C		
590	68.6	898.9	.000229	7.61
639	61.1	899.2	.000221	7.96
729	47.7	898.8	.000196	8.09
871	36.2	898.7	.000178	8.76
1003	29.2	898.8	.000165	9.31
1269	22.3	898.3	.000160	11.44
1815	15.2	898.8	.000156	15.97
2060	13.5	898.1	.000157	18.24
2570	12.3	898.5	.000178	25.89
2925	11.6	898.7	.000192	31.64
3590	11.0	898.5	.000223	45.18
3890	10.8	898.0	.000237	52.03
		Temperature 18.9°C		
500000	7.4	899.4	.0209	590800

The power loss in any portion of an alternating current circuit containing capacity and resistance in series with it is $EI \cos\theta$ where $\cos\theta$ is the power factor. When the loss is small, as in the case of the condensers studied, $\cos\theta = R\omega C$. Hence the power loss is

$$P = E^2 R\omega^2 C^2.$$

In Tables III and IV typical values of the power factor $R\omega C$ and the power loss per unit potential difference applied to the condenser $R\omega^2 C^2$ are given for five of the liquids studied. As will be noted the power loss is not constant as should be true if the loss be due solely to conductivity.

TABLE III

*Values of $R\omega C$**

f	Benzene	Xylene	Toluene	Castor Oil	Olive Oil
600	.00592			.000229	
700	.00512	.00258	.00349	.000203	.000200
800	.00445	.00218	.00293	.000185	.000176
1000	.00338	.00167	.00230	.000166	.000144
1200	.00283	.00136	.00184	.000160	.000122
1500	.00228	.00106	.00148	.000156	.000102
2000	.00168	.000792	.00108	.000159	.0000813
2500	.00133	.000636	.000875	.000175	.0000720
3000	.00109	.000526	.000728	.000194	.0000661
3500	.00091	.000455	.000592	.000220	.0000632
500,000				.0209	

*The article by A. B. Bryan in the October number of the Physical Review appeared after the present article was written. It may be noted that the values of $R\omega C$ as found by the writer do not fit his equation $\psi = \psi_0 + A/f$, which would lead to a straight line if ψ were plotted as a function of $1/f$.

TABLE IV

Power Loss per Unit Voltage
Watts $\times 10^{-10}$

f	Benzene	Xylene	Toluene	Castor Oil	Olive Oil
600	205			7.6	
700	202	102.	138	8.0	7.9
800	200	98.8	132	8.4	7.9
1000	196	94.3	130	9.3	8.1
1200	193	92.1	125	10.4	8.3
1500	191	89.9	125	12.6	8.6
2000	189	89.5	122	18.0	9.2
2500	187	89.9	123	24.6	10.2
3000	186	89.2	123	32.9	11.2
3500	184	90.1	117	43.0	12.5

It has been found by Lawther[5] and verified by McLeod[4] that if the cause of the power loss is dielectric absorption, as in the case of solids, then

$$\log R = \text{const.} - k \log f \qquad (1)$$

[5] H. W. Lawther, Harvard thesis, unpublished

where R is the equivalent series resistance, f the frequency, and $1<k<2$, a result which is in agreement with the theory developed by von Schweidler[2] and others and experimentally confirmed by Tank.[1]

If the loss in liquids is due simply to the leakage current as indicated by the work of Tank, then the condenser with liquid dielectric may be regarded as a pure capacity in parallel with a constant resistance and the impedance will be given by the equation

$$Z=\frac{4\pi d}{A\omega}\ \frac{2\gamma T-j\epsilon}{(2\gamma T)^2+\epsilon^2} \tag{2}$$

where A is the area; d, the distance between plates; ω, 2π times the frequency; T the period of the oscillatory current; γ the conductivity; and ϵ the dielectric constant. From Eq. (2) it is evident that a leaky condenser is the equivalent of a condenser of capacity

$$C_x=\frac{A}{4\pi d}\ \frac{(2\gamma T)^2+\epsilon^2}{\epsilon}\ . \tag{3}$$

and of resistance in series with C_x,

$$R_x=\frac{4d\gamma}{A}\ \frac{T^2}{4\gamma^2\ T^2+\epsilon^2}. \tag{4}$$

The equivalent series capacity C_x is then a linear function of the square of the period, and if the conductivity is so slight that the term $(2\gamma T)^2$ may be neglected in comparison with ϵ^2, C_x reduces to the usual constant value.

The equation for the equivalent series resistance R_x is of the form

$$xy+ay-bx=0 \tag{5}$$

where $x=T^2$, $y=R$, $a=\epsilon^2/4\gamma^2$, $b=d/A\gamma$. This is the equation of an hyperbola with asymptotes parallel to the axes. If the conductivity is so slight that the term $(2\gamma T)^2$ may be neglected in comparison with ϵ^2, Eq. (4) reduces to

$$R_x=(4d\gamma/A\epsilon^2)T^2. \tag{6}$$

Since in the case of most of the oils investigated the capacity was found constant within the experimental errors (see Table I), if the loss be due to conductivity alone the curve plotted with R_x and T^2 as co-ordinates should be a straight line through the origin. Typical curves are shown in Figs. 3, 4 and 6.

With the exception of the curves for castor oil, these are approximately straight lines through the origin, but in practically every case there is a slight deviation. To test whether this deviation might be caused by a progressive error in the measurements due possibly to temperature changes or absorption of moisture, the readings were taken first in the

order from lower to higher frequencies, and then in the reverse order. No difference in the results was noted. Since also the measurement of the resistance of the sputtered film showed any variation with the frequency to be less than the probable experimental error, the regular deviation from the straight line apparently cannot be explained either by a progressive error in the measurement of the resistance or by a progressive change in resistance due either to increase in temperature or to absorption of moisture.

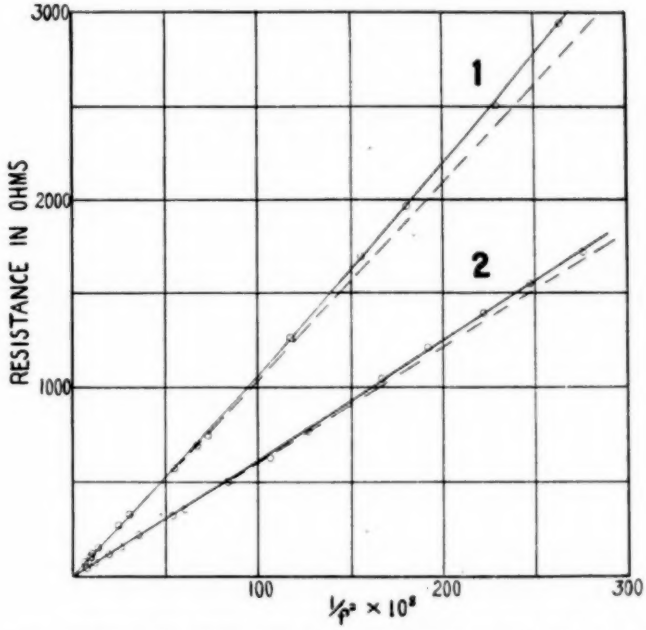

Fig. 3. Equivalent series resistance of the condenser as a function of the square of the period of the oscillatory current. Curve 1, with xylene as dielectric; Curve 2, with benzene.

If, then, the deviation from the straight line represents an actual deviation from the law, it seems probable that there is a small loss due to some cause other than conductivity, which follows a different law of variation with frequency. In confirmation of this view it is to be noted that the deviation varies with the substance and is not proportional to the resistance measured. In the case of castor oil there is some doubt whether the straight line would not fit the points quite as well and in olive oil there is no indication of deviation from the straight line.

Xylene showed the effect more strongly than any other dielectric. In this case it happened that there was a decided change in the equivalent series resistance for the same sample under varying conditions. Fig. 3,

Curve 1, shows a curve obtained when the xylene had been allowed to stand in the condenser for nearly a month. Fig. 4, Curve 1, was obtained after standing about five days. Fig. 4, Curve 2, was obtained after the xylene had been removed from the condenser and almost immediately poured back and again freed from air by pumping. A possible explanation of the marked changes in resistance is that the nickel plating acted as a catalyzing agent to bring about reduction and that exposure to air brought about re-oxidation. In various tests of oils it has been found that the metal of the container has a decided influence upon the amount of oxidation due to the enclosed air.

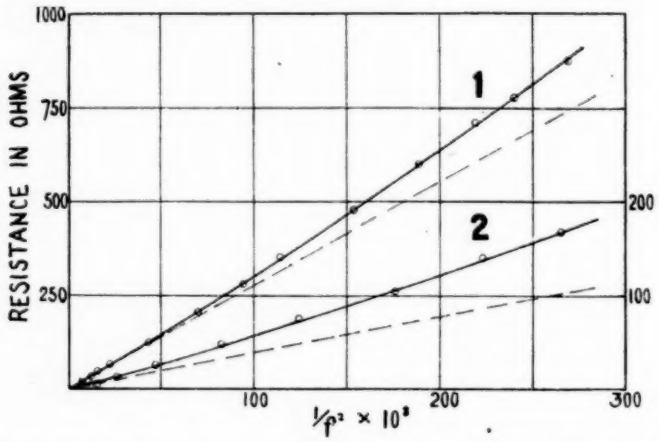

Fig. 4. Equivalent series resistance as a function of the square of the period of the oscillatory current. Curves 1 and 2, xylene.

In order to study the cause of the deviation from the straight line the differences between the experimental curve and the straight line drawn tangentially to the curve at the origin were taken as representing fairly well the equivalent series resistances due to the second cause. A comparison of the three curves for xylene shows that the change in this added resistance is relatively small for a large change in the total series resistance. For a value of the ordinate of 250 ($f=632$) the corresponding values are

Total R_x	δR
2775	160
810	125
155	60

These total resistances are in the ratio 18:5:1, while the differences are in the ratio 2.7:2:1. The difference values are of course only rough approximations because of the difficulty of accurately determining the tangent.

To test the possibility that this deviation might be caused by a slight loss due to dielectric absorption as in solids, the logarithms of the differences were plotted against the logarithms of the corresponding frequencies. The curves obtained for xylene (see Fig. 4) are shown in Fig. 5. The points fit the straight line as well as could be expected, but the value of k differs for the two curves and is greater than 2. Since theory requires k to lie between 1 and 2, the only conclusion to be drawn is that there is in addition to the loss due to the normal conductivity, an apparent loss which varies with the liquid but is for most liquids very small.

Castor oil presented an apparent exception in behavior. When the other dielectrics were used the equivalent series resistance diminished so rapidly that it was found unnecessary to measure the resistance at fre-

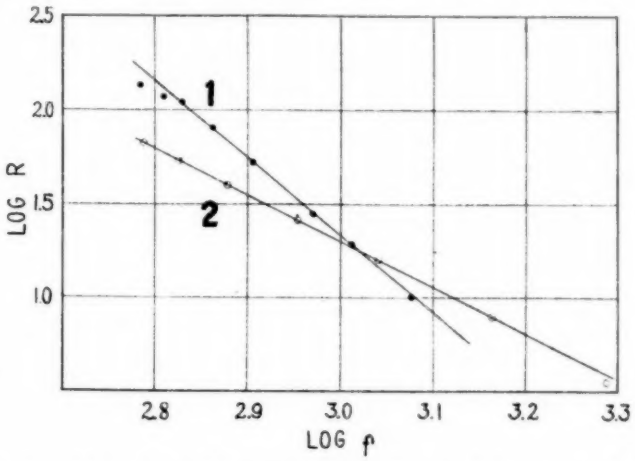

Fig. 5. The logarithm of the difference of the ordinates of the curves of Fig. 4 as a function of the logarithm of the frequency.

quencies above 3700. A few measurements served to indicate that the resistance at high frequencies was of the right order of magnitude, usually a few tenths of an ohm at a frequency of 33,000, but the values obtained were too small to be accurately measured by the method used. With castor oil there was a resistance of several ohms at a frequency of a million or more. The curve plotted for the series resistance as a function of the square of the period for frequencies up to 33,000 cycles would, if prolonged, have cut the axis of resistance at a value in the neighborhood of 9 to 10 ohms for the two samples tested (see Fig. 6, Curve 2). The curve similarly plotted for frequencies above 200,000 cycles is shown in Fig. 6, Curve 1. The experimentally determined points were found to fit fairly well the equation

$$T^2R+6(10)^{-5}\,R-8.7\,T^2=0 \qquad (7)$$

which is the equation for a rectangular hyperbola of the form given in Eq. (5) for a leaky condenser where the conductivity is large in comparison with the dielectric constant. For frequencies below 33,000 cycles the values of the ordinate would be approximately constant and very nearly equal to the intercept on the R-axis of curve 2. Curve 2 may therefore be regarded as the sum of two curves, one the usual curve through the origin. The equation for the total series resistance as a function of the square of the period would then be of the form

$$R=\frac{a_1T^2}{\epsilon_1^2}+\frac{a_2T^2}{b_2T^2+\epsilon_2^2}$$

which would indicate that a condenser with castor oil as the dielectric behaves like two leaky condensers in series. This cannot be explained as

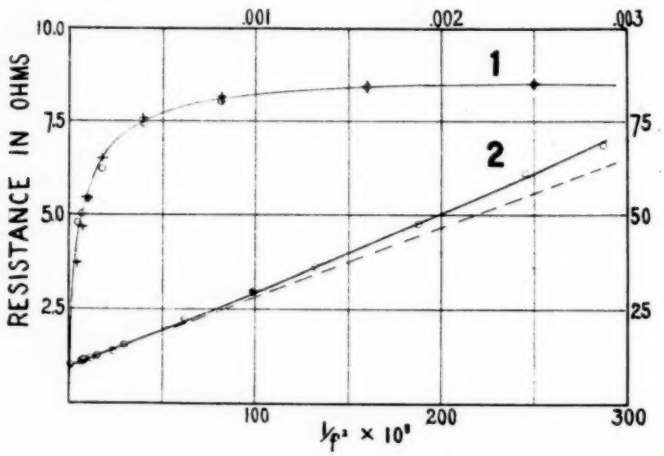

Fig. 6. Equivalent series resistance as a function of the square of the period of the oscillatory current. Curve 1, castor oil at high frequencies (abscissas given above); curve 2, castor oil at low frequencies (abscissas given below). Points indicated with a cross, calculated from Eq. (7); those with a circle, experimentally determined.

due to ordinary impurities, for the effect of these would be to increase the leak and hence to increase the slope of the line through the origin. This was experimentally confirmed in the data obtained in the case of paraffine oil in which the slope of the line through the origin increased as the acid impurity continued to act on the nickel lining, but the curve continued to pass through the origin.

Further to test the question of impurity in the castor oil, about one-half the oil was thoroughly shaken with distilled water in a separatory funnel, and after several days separated. The oil was dried again by gentle heating and new readings taken using this oil. The slope of the curve was slightly lessened, indicating that the oil was perhaps partially purified, but the

curve cut the axis at approximately the same point as before, indicating that the effect in question was not altered. Whether this effect is due to a peculiarity of the castor oil molecule, or more probably to the tendency of the water present to form a more highly conducting film next the metal, must be determined by further experiments. The only other dielectric which showed any trace of the same behavior was olive oil, for which the straight line cut the axis of resistance at a point approximately equal to 1.1 ohms.

It is the intention of the writer to study further the cause of this behavior and if possible to use the law of variation of the equivalent series resistance with the frequency as a basis for the classification of oils and other liquid dielectrics.

The experimental work was carried out during a half year's leave of absence spent in the Cruft Laboratory of Harvard University. The writer wishes to express her appreciation of the courtesy of Harvard University in permitting her to work in the laboratory, and in particular her indebtedness to Professor Pierce, the director of the laboratory, for his kindness in placing at her disposal one of the laboratory problems and for his continued interest in the work, and to Professor E. L. Chaffee for many courtesies.

WELLESLEY COLLEGE,
August 12, 1923.

ACOUSTIC WAVE FILTERS: ATTENUATION AND PHASE FACTORS

By G. W. Stewart

Abstract

Acoustic wave filters; attenuation and phase factors.—*Theoretical discussion.* The ratio of the rate of volume displacements in successive sections e^V is equal to $e^{-\alpha} e^{-i\varphi}$ where α is the attenuation constant and φ the decrease in phase from section to section. If Z_1 and Z_2 are the impedances in the conduit and branch respectively, it is shown that in the region of no attenuation, $\cos \varphi = 1 + \frac{1}{2} Z_1/Z_2$ and φ changes from 0 to π, while in the attenuated region φ is either 0 or π and $\cosh \alpha = |(1 + \frac{1}{2} Z_1/Z_2)|$, becoming infinite for the natural frequency of the side branch while φ passes discontinuously from 0 to π or π to 0. *Experimental values of phase change* φ. Sound from various points along the filter was transmitted to one ear and the relative phase was determined from the apparent direction of the phantom source. For a low-pass filter the values of the total change per section agree well with the theory except that the change occurs gradually instead of suddenly, but agreement was not found in the cases of the other two types.

I. Theoretical

In a recent discussion of acoustic wave filters[1] the theory and experimental results as to frequency limits of transmission without attenuation were presented. The present article is a continuation of the theory, with acknowledgement of the suggestions received from discussions of electric wave filters by Campbell,[2] Pierce[3] and Zobel.[4] The acoustic filters discussed in the previous article[1] were shown diagrammatically in Fig. 2. If Z_1 and Z_2 refer to acoustic impedances, I_n to the rate of volume displacement in the n^{th} section, and $AGEG$ to the conduit through which transmission is desired, it was shown that

$$I_{n+1}/I_n = e^V \tag{1}$$

where

$$\cosh Y = 1 + \tfrac{1}{2} Z_1/Z_2. \tag{2}$$

If

$$e^V = e^{-\alpha} e^{-i\varphi} \tag{3}$$

α is the attenuation constant and φ is the decrease in phase from section to section.

For the practical filters previously discussed[1] the different approximate assumptions made led to different expressions for Z_1 and Z_2 but in all

[1] G. W. Stewart, Phys. Rev. **20**, 528, December, 1922
[2] Campbell, U. S. Patent 1, 227, 113.
[3] Pierce, Chap. XVI, Electrical Oscillations and Electric Waves, 1920
[4] Zobel, Bell Sys. Tech. J. **2**, 1, Jan., 1923

cases the ratio between them was real and therefore cosh Y was real. Hence (cosh $\alpha \cos\varphi + i \sinh \alpha \sin\varphi$) is real, and

$$\sinh \alpha \sin \varphi = 0. \tag{4}$$

Therefore cosh $Y = \cosh \alpha \cos \varphi$. Then when $\alpha = 0$, or *in the region of no attenuation*,

$$\cosh Y = \cos \varphi = 1 + \tfrac{1}{2} Z_1/Z_2. \tag{5}$$

But the former discussion[1] shows that the limits between which $\alpha = 0$, are determined from the relationships, $Z_1/Z_2 = 0$ and $Z_1/Z_2 = -4$. These two ratios, when substituted in (5) give respectively, $\cos \varphi = 1$ and $\cos \varphi = -1$.

It is clear from these that φ changes from zero to π when the frequency is varied from one limit of no attenuation to the other. Since functions of Z_1 and Z_2 employed in our theory are continuous, φ must vary continuously between these frequency limits. *In the attenuated region*, since α is not zero, Eq. (4) shows that $\sin \varphi = 0$, and $\varphi = 0$ or π. These two possible values of φ are the same as those just found at the limits of no attenuation, as they must be for φ is single valued.
Since,

$$\cosh \alpha \cos \varphi = \cosh Y = 1 + \tfrac{1}{2} Z_1/Z_2, \tag{6}$$

we have throughout the attenuated region, the positive quantity

$$\cosh \alpha = (1 + \tfrac{1}{2} Z_1/Z_2)/(\pm 1) > 0 \tag{7}$$

The sign of the sum in the parenthesis (7) is therefore determined by that of $\cos \varphi$. Consequently if it changes sign, $\cos \varphi$ must also, and this means an alteration by π.

The above discussion is identical with the reasoning in the case of electric filters and shows that φ can be obtained from (5) in the unattenuated region and from (6) in the attenuated region, and that in the latter region, α is given by (7).

In discussing the three types of filters previously considered,[1] the same semi-empirical values of Z_1 and Z_2 are adopted. These give for the low-pass, high-pass and single-band filters respectively, the following values of the quantity in Eq. (6):

$$1 + \frac{\frac{1}{2} M_1 C_2 \omega^2}{M_2 C_2 \omega^2 - 1};\ 1 + \frac{\frac{1}{2} M_1}{M_2(1 - M_1 C_1 \omega^2)};\ 1 + \frac{M_1(M_2 C_2 \omega^2 + M_2' C_2 \omega^2 - 1)}{2 M_2(M_2' C_2 \omega^2 - 1)}.$$

If Eqs (5), (6) and (7) are utilized, substituting the values just cited for the right hand member, one can readily ascertain the following:

1. In the region of no attenuation, φ changes with increasing frequency from 0 to π (low-pass), π to 0 (high-pass), 0 to π (single-band-pass); and for all $\cosh \alpha = 1$.

2. With each filter there is in an attenuation region an infinite value of α for a frequency at which φ passes discontinuously, with frequency increasing, from π to 0 (low-pass), 0 to π (high-pass), and π to 0 (single-band-pass). In the last named filter, $\alpha=\infty$ occurs in the upper of the two regions of attenuation.

3. The value of cosh α at zero frequency is $(1+M_1/2M_2)$ for the high-pass and single-band-pass filters. The low-pass has this value at infinite frequency.

4. In the cases of the low-pass and the single-band-pass filters, at the frequency for which $\alpha=\infty$, each filter reduces to the well-known case in acoustics wherein, if the frequency is that causing resonance in the side branch, the transmission through the conduit past the branch is zero.

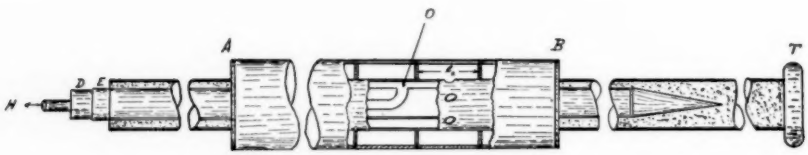

Fig. 1. Low-frequency-pass filter.

II. Experimental

Values of α. A comparison of theoretical and experimental values of α has been made by H. B. Peacock and is published in an accompanying article.

Values of φ. The accompanying diagram shows the low-frequency-pass filter AB and the apparatus for measuring the change in φ. The sound from the telephone T passes through a tube partially filled with hair felt which is continuous with the inner tube of the filter AB. The sound, after leaving the filter, continues to pass through a similar tube containing hair felt and finally either into the atmosphere or, by reflection from the opening, back into the tube. The quantity and distribution of the hair felt were such as to prevent noticeable resonance. The distance from B to T is 100 cm and from A to E is 46 cm. The filter AB is similar in principle to those already described[1] and is, in fact an extension of H13 from 5 sections to 10 sections. The inner case was made of two telescoping tubes, the outer one containing a slot and the inner one a tube with the opening in the slot. By sliding the inner tube D back and forth, the opening of the hearing tube at O could be moved without modifying the phase conditions in the tube other than through the influence of the opening. The sound transmitted into this "feeler" tube was led to one ear of the observer. The current passing through the telephone T passed

also through another telephone T', not shown. T' was shunted by a resistance which remained constant throughout a trial. A tube was presented to the telephone T' and the sound from it was transmitted to the other ear of the observer. The opening of the tube could be moved a small distance nearer to or further from T', thus altering intensity values without an appreciable change in phase. The relative phases in the two tubes were compared by the binaural difference of phase effects.[5] In this effect, at a phase difference zero the phantom source of sound passes

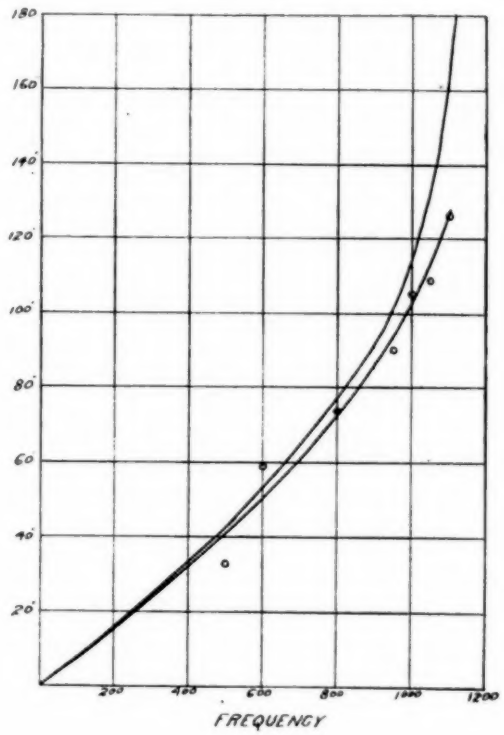

Fig. 2

across directly in front, and at a difference of π it passes quickly from one side to the other. By observing the position of the tube D at these two phase differences, care being taken to keep the intensities approximately constant, the change of phase along the filter could be ascertained. Since each section was 4 cm in length, the results are expressed in Fig. 2 as the change in φ per section, as a function of the frequency. The upper full line curve represents the values computed from (5). The agreement of

[5] The effect is described fully by Stewart, Phys. Rev. **15**, 432, 1920

theory and experiment is satisfactory, excepting in one respect. The theory asserts that φ changes discontinuously at the junction. In point of fact there is strictly no junction "point" and experimentally φ does not change discontinuously. The agreement, even with this exception, is remarkable. In fact, the nature of the assumptions made in the derivation of the theory does not permit one to anticipate that our somewhat empirical expressions for Z_1 and Z_2 would lead to correct theoretical values of φ.

A high-frequency-pass and a single-band filter were constructed and the same exploring tube as shown in Fig. 1 was used in them. The observations, however, failed to disclose any such variation in φ as that determined by (5). At the present time there is offered no explanation for this failure other than the semi-empirical nature of the formulas. A careful investigation as to the actual change in φ will need to be made.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
August 25, 1923.

PREDICTED TRANSMISSION CURVES OF ACOUSTIC WAVE FILTERS

By H. B. Peacock

Abstract

Transmission curves for three acoustic wave filters.—Using the experimental procedure of G. W. Stewart, the energy transmitted as a function of the frequency was determined for a low-frequency-pass, a high-frequency-pass, and a single-band-pass filter. Corrected for dissipation, the results agree well with theoretical curves computed from Stewart's equation for a filter of n sections $I_n/I_0=e^{-n\alpha}$, where α, the attenuation factor, is computed from the impedances.

ACCORDING to the theory developed in the preceding paper by G. W. Stewart to account for the action of certain acoustic wave filters, it should be possible to predict transmission curves from computation. It is the purpose of this investigation to test this theory by comparing the theoretical and experimental transmission curves.

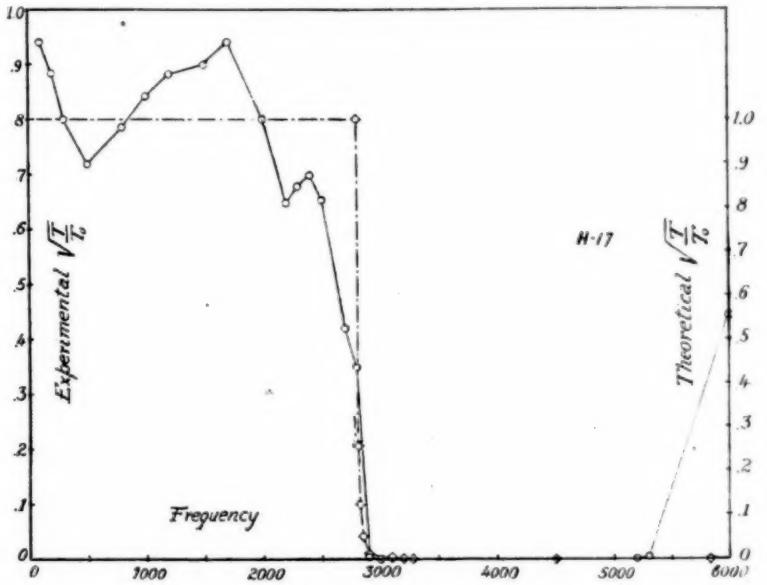

Fig. 1

The experimental procedure was similar to that previously used by G. W. Stewart.[1] Three types of filter were investigated, H-17 being a low-frequency-pass filter, L-50 a high-frequency-pass filter, and SB-9,

[1] Stewart, Phys. Rev. **20**, 528, Dec., 1922

a single-band-pass filter. The experimental curves are the full-line curves shown in Figs. 1, 2, and 3, in which the square-root of the percentage transmission is plotted as a function of the frequency.

The theoretical transmission curves can be determined from the equations,

$$e^{-\alpha} = I_{n+1}/I_n, \tag{1}$$

which becomes $e^{-n\alpha} = I_n/I_0$ for a filter of n sections, where

$$\cosh \alpha = \pm(1+\tfrac{1}{2} Z_1/Z_2). \tag{2}$$

In these equations α is the attenuation factor; the I's are the rates of change of volume displacement and are proportional to the square-root

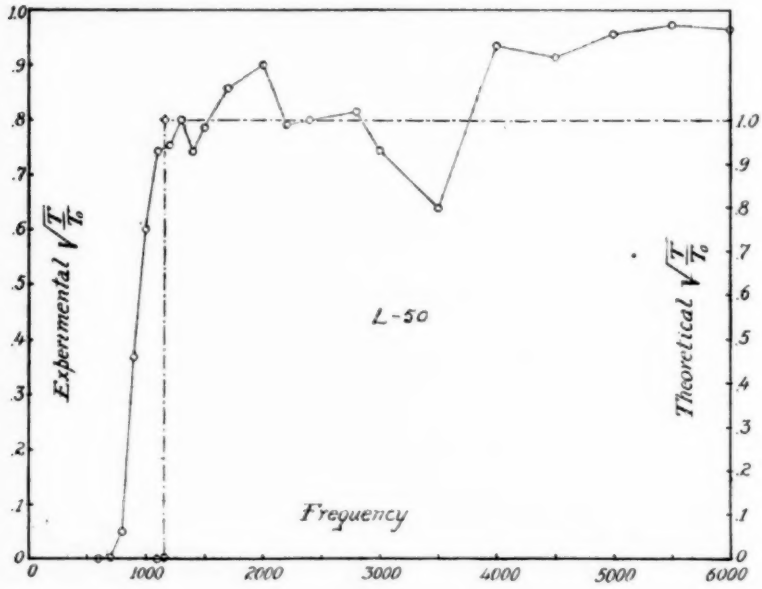

Fig. 2

of the transmitted energy; the Z's are acoustic impedances and can be calculated from the dimensions of the filter and the frequency. The values of Z_1 and Z_2 are those selected by Stewart. The computed transmission curves are shown by the dotted lines in Figs. 1, 2, and 3.

In comparing the two sets of curves, it will be observed that the ordinates of the theoretical and experimental curves are not the same. The reason for this is that these filters do not transmit all of the energy outside of the attenuated region, and this is explained by unavoidable dissipation. However, at a certain frequency for each filter, a sharp diminution of intensity occurs. Since we are chiefly concerned with the comparison with theory within the region of attenuation, the transmitted

energy at the beginning of attenuation is taken as 100 per cent for the theoretical transmission. With the exception of the difference caused by dissipation, the experimental values are in fair agreement with those computed from the formulas.

Considering the necessary approximations in the theory and the inexactness of its application, a perfect correspondence between theory and experiment cannot be expected. The chief approximations are the assumption of infinitely long wave-length and somewhat arbitrary

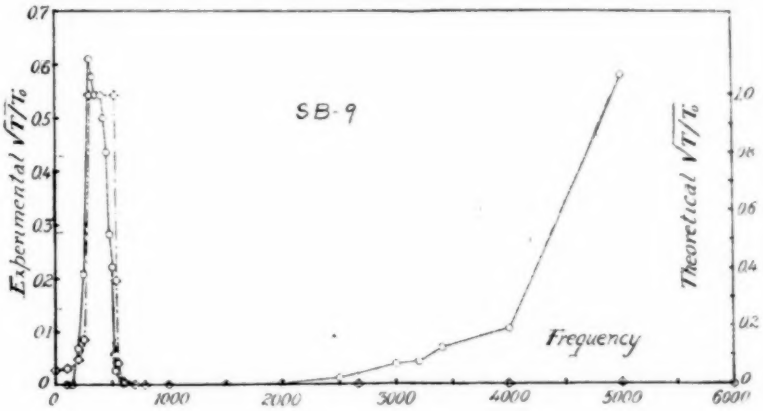

Fig. 3

limiting values for Z_1 and Z_2. Under the circumstances the agreement between theory and experiment is surprisingly good.

In conclusion the writer wishes to express his appreciation of the courtesies extended by the staff of the Department of Physics and to acknowledge especially the assistance received from Dr. G. W. Stewart, under whose direction the experiments were conducted.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
August 25, 1923.

A STUDY OF RELATIVE MOTION IN CONNECTION WITH CLASSICAL MECHANICS

By H. Zanstra

Abstract

Derivation of equations of motion of the second order, containing relative coordinates only.—This article is a continuation of the work of many authors, among others Berkeley, Neumann, Maxwell, Lange, Mach, Boltzmann, Föppl, and Kolkmeyer, whose work is briefly discussed. The main difficulty in Newton's mechanics seems to be to define the system of axes (inertial system) to which the motion is referred. Three solutions have been proposed. Föppl defined the system on a relative basis. Another and apparently more direct solution is to refer the motion of particles to other particles, that is, to use "relative coordinates" in the equations of motion. A third solution would be to obtain invariant equations, the same for all systems of reference. Introducing an hypothesis stated by Föppl, that for a system with its origin at the center of mass the angular momentum of the universe vanishes, invariant equations are obtained from the Newtonian, (though this is sometimes denied to be possible), and they degenerate into the Newtonian form if certain functions of coordinates and velocities occurring in them become zero by a suitable choice of the system of reference. It is believed, however, that such equations do not offer a complete solution of the problem of relativation of motion so as to satisfy the physicist; whereas the introduction of relative coordinates does. In this article this second solution has been applied to the Newtonian theory. Equations of motion are derived by introducing Föppl's hypothesis, which are of the second order and contain relative coordinates only. These equations may be taken as the basis for a complete system of mechanics. As examples the systems of Ptolemy and of Kepler are worked out.

Application of relative coordinates to Einstein's theory of gravitation.—It is believed that the possibility of introducing relative coordinates is not limited to the Newtonian theory. As an example of the application of these coordinates to Einstein's theories, the case of the motion of a heavy and a light particle is considered and it is suggested that an hypothesis similar to Föppl's may give equations of motion into which only the distance apart of the particles measured by an observer on the heavier, enters.

1. *The use of relative coordinates to describe the observed motion.* It is well known that Newton introduced the idea of absolute motion in the system of mechanics he created. At the same time, however, he stated explicitly that the motion of bodies in space, such as we observe, is a relative one. The motion of bodies is given by the position of their parts at different instants, and the observed motion is relative because the observed position is relative. Let us inquire as to the sense in which this is to be understood. We introduce for this purpose the customary idea of a material point, that is of a body or part of a body of small dimensions, which, as far as its position is concerned, may be treated

as a mathematical point. If there is a system of n points ($n>2$), to which our observation is confined, the complete specification of the distances of all these points requires the determination of only $3n-6$ of them, suitably chosen. We might e.g. determine for any three points 1, 2 and 3 the sides of the triangle they form, and for any subsequent point ν the three distances of that point from the corners of that triangle. Some of the distances might be replaced by measured angles between lines joining the points, or between the planes of two adjacent triangles. Our conclusion is then, that the relative position of the n material points (or as is sometimes said: the configuration of the point system) is given by $3n-6$ independent coordinates, to be determined by observation, the term "coordinates" being used in the generalised sense. In every practical case of observation the position of material points is relative in the sense understood here.

Coordinates serving to fix the relative position of material points will be designated as relative coordinates. We aim to solve the difficulties connected with the idea of absolute motion in Newton's mechanics by introducing these relative coordinates in the equations of motion.

2. *An equation of motion in relative coordinates, obtained from the differential equations of Newton's mechanics.* The relative coordinates we are about to introduce in this paragraph are referred to a rectangular system of axes XYZ. This system XYZ is defined in such a way that its origin permanently coincides with any one of the material points, which will be designated as point 1; further we shall pass its axis of X permanently through any second point 2, and the XY plane permanently through any third point 3. There is ambiguity as regards the positive direction of the axis of Y, but if once chosen it remains definite throughout.

We have by the definition of our axes

$$x_1=0, \quad y_1=0, \quad z_1=0, \quad y_2=0, \quad z_2=0, \quad z_3=0. \tag{1}$$

The $3n-6$ independent coordinates, specifying the relative position of n material points, are: x_2, x_3, y_3; and x_ν, y_ν, z_ν for $\nu>3$.

We shall start from the equations of motion of Newton's mechanics:

$$m_\nu \ddot{x}_\nu' = X_\nu', \quad m_\nu \ddot{y}_\nu' = Y_\nu', \quad m_\nu \ddot{z}_\nu' = Z_\nu'. \tag{2}$$

In these equations the force components X_ν', Y_ν' and Z_ν' represent definite functions of the relative coordinates of all the particles (like the force of gravitation), though occasionally they might be definite functions of the time, or the first time derivative of the relative coordinates might occur in them. In our discussions we shall not use the term force in any other sense.

We assume these Eqs. (2) to hold in a system of axes $X'Y'Z'$. We proceed to transform them to the relative system of coordinates XYZ. As we are perfectly free in choosing the direction of the original axes $X'Y'Z'$, we shall take them *momentarily* parallel to the new axes XYZ. The Eqs. (2) are then, transformed:

$$\left.\begin{aligned}
&\ddot{x}_\nu-(\dot{q}z_\nu-\dot{r}y_\nu)-(q^2+r^2)x_\nu+p(qy_\nu+rx_\nu)-2(q\dot{z}_\nu-r\dot{y}_\nu)-a=X_\nu/m_\nu;\\
&\ddot{y}_\nu-(\dot{r}x_\nu-\dot{p}z_\nu)-(r^2+p^2)y_\nu+q(rz_\nu+px_\nu)-2(r\dot{x}_\nu-p\dot{z}_\nu)-b=Y_\nu/m_\nu;\\
&\ddot{z}_\nu-(\dot{p}y_\nu-\dot{q}z_\nu)-(p^2+q^2)z_\nu+r(pz_\nu+qy_\nu)-2(p\dot{y}_\nu-q\dot{x}_\nu)-c=Z_\nu/m_\nu;
\end{aligned}\right\}\quad(3)$$

where a, b, c are the components of the acceleration of the origin of the old system and p, q, r the components of its angular velocity, all with respect to XYZ.

If these Eqs. (3) did not contain the six quantities a, b, c, p, q, r, there would occur in them only relative coordinates. As it stands, however, our problem is not solved, unless we express those quantities in terms of the relative coordinates. But this can readily be done by substituting the six conditions (1) in (3). Carrying out this substitution, we obtain:

$$\left.\begin{aligned}
&\ddot{x}_\nu-(\dot{q}z_\nu-\dot{r}y_\nu)-(q^2+r^2)x_\nu+p(qy_\nu+rz_\nu)-2(q\dot{r}_\nu-r\dot{y}_\nu)-a=X_\nu/m_\nu,\\
&\text{with 2 similar expressions for } y- \text{ and } z-\text{axis.}\quad(\nu=4\ldots n)\\
&\ddot{x}_2-(q^2+r^2)x_2-a=X_2/m_2,\\
&\ddot{x}_3+\dot{r}y_3-(q^2+r^2)x_3+pqy_3+2r\dot{y}_3-a=X_3/m_3,\\
&\ddot{y}_3-\dot{r}x_3-(r^2+p^2)y_3+qpx_3-2r\dot{x}_3-b=Y_3/m_3.
\end{aligned}\right\}\quad(4a)$$

$$\left.\begin{aligned}
&a=-X_1/m_1,\ b=-Y_1/m_1,\ c=-Z_1/m_1,\\
&-\dot{r}x_2+qpx_2-2r\dot{x}_2-b=Y_2/m_2,\ \dot{q}x_2+rpx_2+2q\dot{x}_2-c=Z_2/m_2,\\
&-(\dot{p}y_3-\dot{q}x_3)+r(px_3+qy_3)-2(p\dot{y}_3-q\dot{x}_3)-c=Z_3/m_3.
\end{aligned}\right\}\quad(4b)$$

The substitution has not altered the Eqs. (3) for $\nu>3$. The substitution for $\nu=1$, 2 and 3 gave the last three equations (4a) and the equations (4b).

Recalling that X_ν, Y_ν and Z_ν stand for functions of the relative coordinates, we may look upon the Eqs. (4a) as being $3n-6$ independent relations among the $3n-6$ independent coordinates, mentioned above: x_2, x_3, y_3, x_ν, y_ν, z_ν $(\nu>3)$, containing, moreover, 6 auxiliary quantities a, b, c, p, q, r. But these 6 auxiliary quantities are expressed in terms of the coordinates by means of the differential Eqs. (4b), and when these six quantities are eliminated from (4a) and (4b), we are left with $3n-6$ *independent differential equations for the* $3n-6$ *independent coordinates*, therefore our problem is theoretically solved.

The system of differential equations (4) is of order $6n-9$. [See §8 (a)]. Therefore it can be reduced to $3n-9$ *equations of the second order and 3 equations of the third order* in which only the $3n-6$ independent coordinates occur. For our purpose it is not necessary to make this

reduction. We shall therefore leave equations (4a) and (4b) as they stand. However, we should keep in mind that our point of view forbids that we interpret the six quantities a, b, c, p, q and r as components of absolute acceleration and angular velocity. They are to be regarded merely as auxiliary quantities which can be eliminated.

To describe the observed motion in a system of material points, A. Föppl[1] has suggested the system of axes XYZ as used here, though he did not introduce the relative coordinates in the equations of motion. On the other hand N. H. Kolkmeyer[2] suggested and worked out the idea of eliminating quantities like a, b, c, p, q and r by expressing them in terms of coordinates.

The combination of these two ideas leads to the equations (4a) and (4b), which by their rather simple form and their general nature are suitable for a general discussion.

Kolkmeyer's purpose is (among others) to introduce relativity of motion in Newton's mechanics without an additional assumption. Therefore his work may lead to much the same conclusions as the equations of this paragraph. In the work of the following paragraphs, however, we shall deviate from the basis on which Kolkmeyer has built, by introducing an hypothesis stated by Föppl.

3. *Föppl's hypothesis concerning the world system and its angular momentum.*[1] An *inertial system*[3] will be defined as a system of axes for which the differential equations of Newton's mechanics hold:

$$m_\nu \ddot{x}_\nu' = X_\nu', \quad m_\nu \ddot{y}_\nu' = Y_\nu', \quad m_\nu \ddot{z}_\nu' = Z_\nu'. \quad (\nu = 1 \ldots n) \qquad (2)$$

We assume that there are such inertial systems $X'Y'Z'$. Moreover, we assume with Föppl that the totality of matter in the universe consists of a finite number n of points, so that the undex ν includes all material points in space. Furthermore we suppose that the quantities X', Y', Z' on the righthand side obey the *law of action and reaction* for forces and couples:

$$\left.\begin{aligned} \Sigma X' = 0, \ \Sigma Y' = 0, \ \Sigma Z' = 0, \\ \Sigma(y'Z' - z'Y') = 0, \ \Sigma(z'X' - x'Z') = 0, \ \Sigma(x'y' - y'X') = 0, \end{aligned}\right\} \qquad (5)$$

where Σ includes all n points.

Combining this with (2) and integrating we obtain the equations for conservation of momentum and angular momentum:

$$\left.\begin{aligned} \Sigma m\dot{x}' = T_1, \ \Sigma m\dot{y}' = T_2, \ \Sigma m\dot{z}' = T_3, \\ \Sigma m(y'\dot{z}' - z'\dot{y}') = R_1, \ \Sigma m(z'\dot{x}' - x'\dot{z}') = R_2, \ \Sigma m(x'\dot{y}' - y'\dot{x}') = R_3. \end{aligned}\right\} \qquad (6)$$

[1] A. Föppl, Vorlesungen über technische Mechanik, VI, Erster Abschnitt, Die relative Bewegung.

[2] N. H. Kolkmeyer. Eliminatie van de begrippen assenstelsel, lengte en tijd uit de vergelijkingen voor de planetenbewegingen. Thesis Amsterdam 1915.

[3] This term was introduced by Lange. See §9.

The inertial system $X'Y'Z'$ can be chosen in such a way that its origin coincides permanently with the center of mass of the total system, as this restriction does not violate Eqs. (2). Such an inertial system with origin permanently at the center of mass is defined as a *principal system of reference* (Hauptbezugssystem):

$$\Sigma mx' = 0, \ \Sigma my' = 0, \ \Sigma mz' = 0. \tag{7}$$

From (7) it follows that in such a principal system $X'Y'Z'$: $T_1 = T_2 = T_3 = 0$. In ordinary mechanics the other three constants then depend upon the distribution of velocities in the universe and are not, in general, zero, unless a special hypothesis about this velocity distribution is made.

This *hypothesis* has been made by *Föppl*: *For a principal system of reference the angular momentum of the universe vanishes, that is:*

$$\Sigma m(y'\dot{z}' - z'\dot{y}') = 0, \ \Sigma m(z'\dot{x}' - x'\dot{z}') = 0, \ \Sigma m(x'\dot{y}' - y'\dot{x}') = 0. \tag{8}$$

Föppl's hypothesis was originated for the purpose of defining inertial systems without making use of the idea of absolute motion.[4] In this way he gave a solution of the difficulties arising from this idea in Newton's mechanics. Another way of solving these difficulties is by introducing relative coordinates in the equation of motion; and Föppl's hypothesis, though not necessary for a solution (see §2), may be of great help in simplifying this problem.

We wish to illustrate this by the following problem:

To relativate the motion if the total system consists of two material points of masses m_1 and m_2, exerting on each other a force which is a function $f(r)$ of their distance r and directed along the line joining them.

We take the inertial system $X'Y'Z'$, to which the motion in ordinary mechanics is referred, with its origin permanently at the center of gravity G of the point system. Then the velocity vectors of the two particles have opposite directions.

Föppl's hypothesis states that in such a principal system of reference the total angular momentum vanishes which is only possible if the velocity vectors of both points are directed along the line joining m_1 and m_2. The motion can therefore be described as taking place along the axis of X. The equations of motion become then

$$m_1\ddot{x}_1' = f(r), \text{ and } m_2\ddot{x}_2' = -f(r).$$

Since, moreover, $x_1' - x_2' = r$, and therefore $\ddot{x}_1' - \ddot{x}_2' = \ddot{r}$, we have

$$m_{12}\ddot{r} = f(r), \tag{I}$$

where $m_{12} = m_1m_2/(m_1+m_2)$. This is the equation of motion, containing the only relative coordinate r, which fixes the relative position of the points (§1).

[4] See §6.

If Föppl's hypothesis is not introduced, we obtain instead of (I) the more complicated expression:

$$m_{12}\ddot{r}=f(r)+R^2/m_{12}r^3 \tag{II}$$

where R is the magnitude of the angular momentum of the system with respect to G. This constant can either be expressed in terms of r and $\ddot{r}$ at one instant or be removed by differentiation. In the latter case the equation of motion becomes

$$m_{12}(\dddot{r}r+3\ddot{r}\dot{r})+[3f(r)+rf'(r)]\dot{r}=0, \tag{III}$$

which is of the *third* order, as might be expected according to §2. On the other hand, Föppl's hypothesis enabled us to derive the Eq. (I) which is of the *second* order.

4. *The equations of motion in relative coordinates, modified by introducing Föppl's hypothesis.* We shall proceed to modify the equations of motion (4a) and (4b) of the general case, by introducing in the derivations of §2 *Föppl's* hypothesis as an additional assumption. For the sake of convenience we shall take the inertial system $X'Y'Z'$, from which we started in §2, as a principal system (see §3):

$$\Sigma mx'=0,\ \Sigma my'=0,\ \Sigma mz'=0. \tag{7}$$

Föppl's hypothesis is then expressed by

$$\Sigma m(y'\ddot{z}'-z'\ddot{y}')=0,\ \Sigma m(z'\ddot{x}'-x'\ddot{z}')=0,\ \Sigma m(x'\ddot{y}'-y'\ddot{x}')=0. \tag{8}$$

In the derivation we carried out in §2 p, q and r represent the components of the angular velocity of the original system with reference to the new system XYZ. From (7) it follows that its origin has the coordinates $\Sigma mx/\Sigma m$, $\Sigma my/\Sigma m$, $\Sigma mz/\Sigma m$. In view of this the additional condition (8) becomes

$$\begin{aligned}&p[\Sigma m\Sigma m(y^2+z^2)-(\Sigma my)^2-(\Sigma mz)^2]-q(\Sigma m\Sigma mxy-\Sigma mx\Sigma my)\\&-r(\Sigma m\Sigma mzx-\Sigma nz\Sigma mx)=\Sigma m\Sigma m(y\dot{r}-z\dot{y})-(\Sigma my\Sigma m\dot{z}-\Sigma mz\Sigma m\,\dot{y}),\end{aligned} \tag{9}$$

with two similar expressions for the y- and z-axis.

These equations give us p, q and r as functions of the relative coordinates and their first derivatives. These functions may be substituted in the equations (4a) and (4b) of §2 and then the quantities $\dot{p}$, $\dot{q}$, $\dot{r}$ and a, b, c eliminated. We shall not carry out this process (apart from the

rather trivial elimination of a, b and c), but put the result in a form such as to indicate the elimination. The result is:

$$\left.\begin{aligned}
&\ddot{x}_\nu-(\beta z_\nu-\gamma y_\nu)-(q^2+r^2)x_\nu+p(qy_\nu+rz_\nu)-2(q\dot{z}_\nu-r\dot{y}_\nu)=\frac{X_\nu}{m_\nu}-\frac{X_1}{m_1},\\
&\quad\text{with two similar expressions for } y\text{- and } z\text{-axis}\quad(\nu=4\ldots n)\\
&\ddot{x}_2-(q^2+r^2)x_2=\frac{X_2}{m_2}-\frac{X_1}{m_1},\\
&\ddot{x}_3+\gamma y_3-(q^2+r^2)x_3+pqy_3+2r\dot{y}_3=\frac{X_3}{m_3}-\frac{X_1}{m_1},\\
&\ddot{y}_3-\gamma x_3-(r^2+p^2)y_3+qpx_3-2r\dot{x}_3=\frac{Y_3}{m_3}-\frac{Y_1}{m_1}.
\end{aligned}\right\}\quad(10a)$$

where:

$$\left.\begin{aligned}
&-\gamma x_2+qpx_2-2r\dot{x}_2=\frac{Y_2}{m_2}-\frac{Y_1}{m_1},\quad \beta x_2+rpx_2+2q\dot{x}_2=\frac{Z_2}{m_2}-\frac{Z_1}{m_1},\\
&-(\alpha y_3-\beta x_3)+r(px_3+qy_3)-2\ p\dot{y}_3-q\dot{x}_3)=\frac{Z_3}{m_3}-\frac{Z_1}{m_1},
\end{aligned}\right\}\quad(10b)$$

$$\left.\begin{aligned}
&p[\Sigma m\Sigma m(y^2+z^2)-(\Sigma my)^2-(\Sigma mz)^2]-q(\Sigma m\Sigma mxy-\Sigma mx\Sigma my)\\
&-r(\Sigma m\Sigma mzx-\Sigma mz\Sigma mx)=\Sigma m\Sigma m(y\dot{z}-x\dot{y})-(\Sigma my\Sigma m\dot{z}-\Sigma mz\Sigma m\dot{y}),\\
&\text{with two similar expressions for } y\text{- and } z\text{-axis.}
\end{aligned}\right\}\quad(10c)$$

This way of writing the equations is quite equivalent to the process of elimination described above. As before, α, β, γ, p, q and r must be considered as auxiliary quantities; they should be solved for from (10b) and (10c) and substituted in (10a), which is possible in view of the fact that (10b) are linear in α, β, γ, and (10c) in p, q, and r.

This leads to *3n−6 differential equations which are all of the second order* and contain only the 3n−6 coordinates and their derivatives. We were unable to obtain such a result in §2 where Föppl's hypothesis was not introduced.

Eqs. (10) are derived from the Newtonian Eqs. (2) and Föppl's conditions (7) and (8). All the mathematical processes of the derivation are reversible. This is not immediately obvious for the elimination of $\dot{p}$, $\dot{q}$ and $\dot{r}$ by putting $\dot{p}=\alpha$, $\dot{q}=\beta$, $\dot{r}=\gamma$. However it is proved in §8b, that the Eqs. (10) imply that

$$\alpha=\dot{p}\quad\beta=\dot{q}\quad\gamma=\dot{r},\qquad(11)$$

therefore the whole mathematical process is reversible. In other words, the Eqs. (10) are the analytical equivalent of Newton's equations (2) with Föppl's conditions (7) and (8).

The points 1, 2 and 3, by which the system of axes XYZ is fixed, are quite arbitrary. Therefore the Eqs. (10), transformed to a system of axes fixed by three other material points k, l and m, remain the same, only the indices 1, 2 and 3 should be replaced by k, l and m. This can be proved directly from Eqs. (10) by transformation.

5. *The equations in vector form. Application to a rigid body.* The first three Eqs. (10a) and Eqs. (10c) can be written in vector form. This cannot be done for the other equations, because of the asymmetry arising from the definition of the system of coordinates XYZ. If $\mathbf{r}_\nu$ represents the radius vector of the point ν, with components x_ν, y_ν, z_ν, and $\mathbf{F}_\nu$ the force on point ν, components X_ν, Y_ν, Z_ν, the *equations in vector form* become

$$\ddot{\mathbf{r}}_\nu - \mathbf{a}\times\mathbf{r}_\nu + \mathbf{w}\times(\mathbf{w}\times\mathbf{r}_\nu) - 2\mathbf{w}\times\dot{\mathbf{r}}_\nu = \frac{\mathbf{F}_\nu}{m_\nu} - \frac{\mathbf{F}_1}{m_1}, \tag{10a}$$

where $\mathbf{a}$, components α, β, γ, and $\mathbf{w}$, components p, q, r are given by (10b) and

$$\Sigma m \Sigma \mathbf{r}\times m(\mathbf{w}\times\mathbf{r}) - \Sigma m\mathbf{r}\times\Sigma m(\mathbf{w}\times\mathbf{r}) = \Sigma m\Sigma\mathbf{r}\times m\dot{\mathbf{r}} - \Sigma m\mathbf{r}\times\Sigma m\dot{\mathbf{r}}. \tag{10c}$$

The sign $\times$ designates a vector product.

There is no harm in writing down the vector Eqs. (10a) for all the n points, if the additional coordinates x_1, y_1, z_1, y_2, z_2, z_3, which are all zero, are introduced. But then the number of coordinates is no longer the minimum number $3n-6$.

The equation (11) in vector form becomes:

$$\mathbf{a} = \dot{\mathbf{w}} \tag{11}$$

In the special case in which the material points 1, 2 and 3 are three points of a *rigid body*, the equations of motion (10) can be reduced to

$$\ddot{\mathbf{r}}_\nu - \mathbf{a}\times\mathbf{r}_\nu + \mathbf{w}\times(\mathbf{w}\times\mathbf{r}_\nu) - 2\mathbf{w}\times\dot{\mathbf{r}}_\nu = \frac{\mathbf{F}_\nu}{m_\nu} - \frac{\mathbf{F}_1}{m_1}, \tag{12a}$$

where $\mathbf{a}$, components α, β, γ and $\mathbf{w}$, components p, q, r are given by

$$\left.\begin{aligned} -A\alpha + (C-B)qr &= L, \\ -B\beta + (A-C)r\dot{p} &= M, \\ -C\gamma + (B-A)pq &= N. \end{aligned}\right\} \tag{12b}$$

$$\Sigma m \Sigma \mathbf{r}\times m(\mathbf{w}\times\mathbf{r}) - \Sigma m\mathbf{r}\times\Sigma m(\mathbf{w}\times\mathbf{r}) = \Sigma m\Sigma\mathbf{r}\times m\dot{\mathbf{r}} - \Sigma m\mathbf{r}\times\Sigma m\dot{\mathbf{r}}. \tag{12c}$$

This result can be obtained either by restricting the general equations (10) (See §8 c) or by replacing equation (4b) of §2 by Euler's dynamical equations for the angular velocity, components $-p$, $-q$, $-r$.

The index 1 at the right hand side refers to the material point at the origin of the system of coordinates. All the other indices ν refer to the material points in space outside the body of reference. The axes X, Y and Z are parallel to the principal axes of inertia; A, B and C represent the principal moments of inertia; L, M and N the components of the external moment.

6. *The system of relative mechanics founded on the equations of motion obtained. Ptolemy's system. Kepler's system. Newton's system with Föppl's conditions.* The general equations (10) in relative coordinates,

obtained in §5, can be *postulated as the fundamental equations for a system of mechanics*. They hold for the motion of any material point ν in space, e.g. for a "fixed" star as well as for a body on the earth. The three material points 1, 2 and 3, through which the system of axes XYZ is chosen, are quite arbitrary; this system may be laid through the sun and two stars, but it may be fixed to a ship, a train, an elevator, or an airplane performing acrobatic stunts, just as well. One might even refer the motion to a part of his own body, e.g. his head. This is perhaps the most direct system of reference in the sense that it corresponds most closely to the conception of bodies in space and their motion which we derive from our visual sensations.

Observations, however, are mostly made with instruments mounted in a laboratory or observatory, which is rigidly connected with the earth. For this reason we shall give some special attention to the case in which the system of reference XYZ is fixed to the earth, which leads to the conception known as *Ptolemy's system*.

Ptolemy's system. We assume:

(1) That the vectors $\mathbf{F}_\nu$, components X_ν, Y_ν, Z_ν, are the same as in the Newtonian theory.

(2) That the earth with sufficient accuracy may be considered as a rigid body.

(3) That there is a distance r_0 beyond which the relative rotation of the lines joining the observer with the stars becomes of lower order of magnitude compared with the motions we are dealing with.

The third assumption is an extension of an experimental fact to those cases in which the stars have not yet been observed, either on account of their being too far away, or because the amount of light emitted is too small. Stars at a distance r, larger than r_0, from the observer are indicated as "distant" stars, the remaining ones as "nearby."

Assumption 2, when applied to the centre of gravity G of the earth, gives from equation (10a)

$$\mathbf{F}_G/m_G-\mathbf{F}_1/m_1=-\dot{\mathbf{w}}\times\mathbf{r}_G+\mathbf{w}\times(\mathbf{w}\times\mathbf{r}_G), \tag{13}$$

where, in virtue of (11), $\mathbf{a}$ has been replaced by $\mathbf{w}$. Moreover, it justifies the use of Eq. (12) for a rigid body.

Eq. (12c), together with assumption 3, enables us to express $\mathbf{w}$ in terms of observed motions. The radius vectors of all distant stars in XYZ have the same angular velocity $\mathbf{u}$ and angular acceleration $\dot{\mathbf{u}}$, apart from deviations of higher order (Assumption 3). For stars nearby there is a deviation $\Delta\mathbf{u}$ from this value $\mathbf{u}$. The equation (12c) becomes therefore

$$\Sigma m\Sigma\mathbf{R}\times m(\mathbf{w}\times\mathbf{R})=\Sigma m\Sigma\mathbf{R}\times m(\mathbf{u}\times\mathbf{R})+\Sigma m\Sigma\mathbf{R}\times m(\Delta\mathbf{u}\times\mathbf{R}) \tag{14}$$

where $\mathbf{R}_\nu=\mathbf{r}_\nu-\Sigma m\mathbf{r}/\Sigma m$.

Observation shows that the number of these nearer stars having appreciable $\Delta\mathbf{u}$ is very small compared with the number of distant stars, and in general the $\mathbf{R}_\nu$ is of the same order. Neglecting for this reason the last term of the righthand side, Eq. (14) reduces to

$$\mathbf{u}=\mathbf{w}, \tag{15}$$

which means that, apart from deviations of a higher order, the auxiliary quantity $\mathbf{w}$ is equal to the angular velocity $\mathbf{u}$ of the system of distant stars.

Replacing (12c) by (15), the equation of motion (12) for the motion referred to a rigid body becomes in virtue of (13) and (11):

$$\ddot{\mathbf{r}}_\nu-\dot{\mathbf{u}}\times\mathbf{r}_\nu+\mathbf{u}\times(\mathbf{u}\times\mathbf{r}_\nu)-2\mathbf{u}\times\dot{\mathbf{r}}_\nu=\mathbf{F}_\nu/m_\nu-\mathbf{F}_G/m_G-\dot{\mathbf{u}}\times\mathbf{r}_G+\mathbf{u}\times(\mathbf{u}\times\mathbf{r}_G), \tag{16a}$$

where

$$\left.\begin{aligned} -A\dot{p}+(C-B)qr&=L,\\ -B\dot{q}+(A-C)rp&=M,\\ -C\dot{r}+(B-A)pq&=N. \end{aligned}\right\} \tag{16b}$$

where p, q and r represent the components of $\mathbf{u}$; A, B and C, the principal moments of inertia of the earth, and L, M, and N, the components of the external moment of force on the earth.

Eqs. (16b) are Eu!er's dynamical equations, with the only difference that p, q and r have the signs changed. They give therefore, for the alteration of $\mathbf{u}$ (p, q, r), the usual precession and nutation of the Newtonian theory. The sign, however, is reversed, as we do not deal with motion of the earth, but with the motion of the distant stars with respect to the earth.

The remaining Eq. (16a) may be written

$$\ddot{\mathbf{r}}_\nu=\dot{\mathbf{u}}\times\mathbf{r}_\nu-\mathbf{u}\times(\mathbf{u}\times\mathbf{r}_\nu)+2\mathbf{u}\times\dot{\mathbf{r}}_\nu+\frac{\mathbf{F}_\nu}{m_\nu}-\frac{\mathbf{F}_G}{m_G}-\dot{\mathbf{u}}\times\mathbf{r}_G+\mathbf{u}\times(\mathbf{u}\times\mathbf{r}_G). \tag{17}$$

The complex motion, given by this equation, may be interpreted as consisting of a number of simpler motions, superimposed kinematically. Table I gives this interpretation for different bodies ν, considered as material points.

The first three terms of the acceleration $\ddot{\mathbf{r}}_\nu$ can be made to disappear by giving to the new system of axes an angular velocity $-\mathbf{u}$, angular acceleration $-\dot{\mathbf{u}}$. They are accordingly interpreted as a rotation $\mathbf{u}$. The other terms are interpreted in a similar way. We notice that the rotation of the pendulum plane in Foucault's experiment and the daily motion of celestial bodies are represented by the same term. For planets we obtain, besides daily motion, precession and nutation, a kind of epicyclic motion consisting of two superimposed elliptical motions, with corrections for the influence of other planets. The second

ellipse of this epicyclic motion follows from the same term as the yearly parallax. Daily parallax for celestial bodies and centrifugal acceleration of a body on the earth are represented by the term d, which is numerically the same for all bodies. They are therefore identical motions. Forces not due to gravitation have a place in the system; they may work on bodies on the earth or on celestial bodies. No effects different from those of the Newtonian theory are obtained, as might be expected.

TABLE I.

PTOLEMY'S SYSTEM

Contribution of each of the components of the acceleration of a point ν.

Body	$a = \dot{\mathbf{u}} \times \mathbf{r}_\nu$	$b = -\mathbf{u} \times (\mathbf{u} \times \mathbf{r}_\nu) + 2u \times \dot{\mathbf{r}}$	$c = \mathbf{F}_\nu/m_\nu - \mathbf{F}_G/m_G$	$d = -\dot{\mathbf{u}} \times \mathbf{r}_G + \mathbf{u} \times (u \times \mathbf{r}_G)$
star	precession and nutation	daily motion	proper motion and yearly parallax	daily parallax
sun	"	"	elliptical orbit, with corrections for influence of planets.	"
planets		"	first ellipse, with corrections for planets; second ellipse, same for all planets, with corr. — corrected epicyclic motion	"
moon	"	"	elliptic orbit, with corrections for influence of sun and planets	"
bodies on earth	"	rotation of pendulum plane in Foucault's exp., deviation of falling bodies, of projectiles, etc.	acceleration of gravity influence of sun and moon: tides. Influence of all other forces $\mathbf{F}_\nu$, on body ν, not due to gravity.	centrifugal acceleration (time of swing of pendulum)

Kepler's system. The sun is taken as origin (point 1) of the system XYZ and the direction of the axes is fixed by two distant stars 2 and 3. We make, as before, assumptions 1 and 3. In the system XYZ the radius vectors of all distant stars have zero rotation, apart from deviations of higher order. For nearer stars let this rotation be $\Delta\mathbf{u}$. From equation (10c) we obtain, then, in the same way as for *Ptolemy's* system the Eq. (15), which leads to

$$\mathbf{u} = \mathbf{w} = 0.$$

Substituting this in the Eqs. (10a), we obtain, apart from deviations of a higher order

$$\ddot{\mathbf{r}}_\nu = \mathbf{F}_\nu/m_\nu - \mathbf{F}_s/m_s, \tag{18}$$

where S stands for the center of the sun. This is the usual equation of motion for planets in Kepler's system.

Newton's system with Föppl's conditions. In this paragraph we take the point of view of the observer. He uses relative coordinates to describe the observed motion and for him, the equations of motion (10) in relative coordinates are therefore fundamental.

The observer may define a new system $X'Y'Z'$ in the following way. Let the radius vector of the origin of $X'Y'Z'$ be $\mathbf{r}_i$, its rotational velocity $\mathbf{w}_i$, both referred to the fundamental system XYZ. Then these quantities are given by:

$$\mathbf{r}_i = \Sigma m\mathbf{r}/\Sigma m, \tag{19a}$$

$$\Sigma m \Sigma \mathbf{r} \times m(\mathbf{w}_i \times \mathbf{r}) - \Sigma m\mathbf{r} \times \Sigma m(\mathbf{w}_i \times \mathbf{r}) = \Sigma m \Sigma \mathbf{r} \times m\dot{\mathbf{r}} - \Sigma m\mathbf{r} \times \Sigma m\dot{\mathbf{r}}. \tag{19b}$$

The fundamental equations (10), referred to these new axes $X'Y'Z'$ become then:

$$m_\nu \ddot{\mathbf{r}}_\nu' = \mathbf{F}_\nu' \tag{20}$$

where moreover from (19a) and (19b) follow the conditions:

$$\Sigma m\mathbf{r}' = 0, \qquad \Sigma \mathbf{r}' \times m\dot{\mathbf{r}}' = 0. \tag{21}$$

This can be proved by performing the mathematical operations of §5 in the reverse order.

Eqs. (20) are the Newtonian equations (2); Eqs. (21) are Föppl's conditions (7) and (8).

In this way the observer has defined a system for which Newton's equations hold (inertial system) entirely in terms of relative coordinates, in which the observed motion is expressed. In a similar way Föppl[1] defined an inertial system on an entirely relative basis, though he did not have the equations in relative coordinates from which to start.

7. *Newton's equations of motion, transformed to an invariant form. Applications to special systems of axes.* When we take the standpoint that mechanics should deal with observed motions (§1), there are certain *difficulties* connected with the *definition of the system of axes*, if *Newton's* mechanics in its original form is used.

These difficulties may be removed in different ways:

(1) By defining the inertial systems in terms of observed motions, consequently on a relative basis. Such a solution by Föppl was mentioned in the preceding paragraph.

(2) By introducing the relative coordinates, in which the observed motion is expressed, in the equations of motion. A satisfactory solution was given by equations (10).

A third solution is obtained by writing down the *equations of motion in an invariant form*. Then the system of axes needs no specification at all.

The Newtonian equations of motion

$$m_\nu \ddot{\mathbf{r}}_\nu' = \mathbf{F}_\nu', \tag{20}$$

together with Föppl's conditions

$$\Sigma m\mathbf{r}' = 0, \qquad \Sigma \mathbf{r}' \times m\dot{\mathbf{r}}' = 0, \tag{21}$$

are transformed to an *arbitrary system of axes* XYZ. Then the following equations are obtained:

$$\ddot{\mathbf{r}}_\nu - \dot{\mathbf{w}} \times \mathbf{r}_\nu + \mathbf{w} \times (\mathbf{w} \times \mathbf{r}_\nu) - 2\mathbf{w} \times \dot{\mathbf{r}}_\nu - \ddot{\mathbf{s}}_\nu = \frac{\mathbf{F}_\nu}{m_\nu}, \tag{22a}$$

$$\mathbf{s} = \Sigma m\mathbf{r}/\Sigma m, \tag{22b}$$

$$\Sigma m \Sigma \mathbf{r} \times m(\mathbf{w} \times \mathbf{r}) - \Sigma m\mathbf{r} \times \Sigma m(\mathbf{w} \times \mathbf{r}) = \Sigma m \Sigma \mathbf{r} \times m\dot{\mathbf{r}} - \Sigma m\mathbf{r} \times \Sigma m\dot{\mathbf{r}}. \tag{22c}$$

In these equations $\mathbf{r}_\nu$ (x_ν, y_ν, z_ν) is the radius vector of point ν in the new system of axes, $\mathbf{s}$ the radius vector of the origin of $X'Y'Z'$ and $\mathbf{w}$ its angular velocity, both referred to XYZ. Regarding, however, $\mathbf{s}$ and $\mathbf{w}$ as auxiliary quantities, which are to be solved for from (22b) and (22c) and substituted in (22a), the $3n$ equations (22) contain the $3n$ coordinates of the material points only. They are therefore *equations of motion* and, as the system of axes XYZ is quite arbitrary, these equations are *invariant*.

Eqs. (22) hold for all systems of reference possible. For this reason it is convenient to use them as a starting point for a discussion of all special systems of axes.

A system of axes can be specified by restricting conditions. By introducing these conditions in (22) the equations of motion for that special system of axes are obtained. Of course it may be that the equations thus obtained can be simplified by purely analytical operations; the method of procedure does not ascertain the simplest form possible.

If our purpose in specifying the system of axes is to obtain a simple form of the equations of motion, a restriction which almost immediately suggests itself is

$$\Sigma m\mathbf{r} = 0, \qquad \Sigma \mathbf{r} \times m\dot{\mathbf{r}} = 0,$$

which is Föppl's definition of a *principal system of reference*. The equation reduces then to the Newtonian form $m_\nu \ddot{\mathbf{r}}_\nu = \mathbf{F}_\nu$.

But we might wish to refer our motion to the *principal axes of inertia of the universe*; the restricting conditions are then:

$$\left.\begin{array}{lll} \Sigma mx = 0, & \Sigma my = 0, & \Sigma mx = 0, \\ \Sigma myz = 0, & \Sigma mzx = 0, & \Sigma mxy = 0, \end{array}\right\} \tag{23}$$

which, introduced in (22), lead to the equations of motion:

$$\left.\begin{aligned} &\ddot{\mathbf{r}}_\nu-\dot{\mathbf{w}}\times\mathbf{r}_\nu+\mathbf{w}\times(\mathbf{w}\times\mathbf{r}_\nu)-2\bar{\mathbf{w}}\times\dot{\mathbf{r}}_\nu=\frac{\mathbf{F}_\nu}{m_\nu}, && (24a)\\ &\text{where the components } p, q, \text{ and } r \text{ of } \mathbf{w} \text{ are given by} \\ &p=\frac{M_x}{I_x},\quad q=\frac{M_y}{I_y},\quad r=\frac{M_z}{I_z}. && (24b)\end{aligned}\right\}\quad(24)$$

M_x, M_y, M_z represent the components of the angular momentum of the universe and I_x, I_y, I_z its principal moments of inertia.

Finally, the need of being as close to the observations as possible might induce us to introduce *relative coordinates* as those of §2. The restricting conditions are then:

$$x_1=0,\ y_1=0,\ z_1=0,\ y_2=0,\ z_2=0,\ z_3=0; \qquad (3)$$

and this leads in a rather simple way to the equations of motion (10) in relative coordinates.

The main use of invariant equations seems to be that they shorten the analytical procedure in cases such as the examples given here. Besides this, they offer a solution of the difficulties connected with the definition of the system of axes in ordinary Newtonian mechanics. This solution, however, can not be regarded as a relativation of motion such as is required by observation (see §1).

8. *Proof of some of the theorems used. Case of plane motion.* Of some statements made the proof will be given here. In general all equations used are in vector form (see §5).

a. *Order of the system of Eqs. (4) of §2.* There are $3n-6$ coordinates occurring in the $3n-6$ equations (4a) of the second order; morover, we have the six auxiliary quantities, occurring in three ordinary equations and three differential equations of the first order (4b). The system consisting of (4a) and (4b) is therefore of order $2(3n-6)+3=6n-9$.

b. *Proof that equations (10) contain the conclusion*

$$\alpha=\dot{p},\quad \beta=\dot{q},\quad \gamma=\dot{r},\quad \text{or}\quad \mathbf{a}=\dot{\mathbf{w}}. \qquad (11)$$

Without going back to the original derivation of (10), Eq. (11) can be proved to be a direct consequence of Eqs. (10a) and (10c). One may convince himself of this by applying the operation $\Sigma m\,\Sigma_\nu\,\mathbf{r}_\nu\times m_\nu$ to equation (10a) written as $\bar{\varphi}=\mathbf{F}_\nu/m_\nu-\mathbf{F}_1/m_1$, and the operation $\dot{\bar{\gamma}}-\mathbf{w}\times\bar{\gamma}$ to equation (10c) written as $\boldsymbol{\gamma}=0$. Two other equations are thus obtained. The right hand side of the first equation, in view of the law of action and reaction (§3), becomes equal to $-\Sigma m(\Sigma m\ \mathbf{r}\times)\ \mathbf{F}_1/m_1$, which by (10a) can be put in the form $(\Sigma m\ \mathbf{r}\times)\ \Sigma m\bar{\varphi}$. After applying the rule of vector algebra $\mathbf{a}\times(\mathbf{b}\times\mathbf{c})+\mathbf{b}\times(\mathbf{c}\times\mathbf{a})+\mathbf{c}\times(\mathbf{a}\times\mathbf{b})=0$, the only difference between the two equations is that the first one has $\mathbf{a}$, where the second

one has $\dot{\mathbf{w}}$. Therefore the $\mathbf{a}$, solved from equation 1, gives the same value as $\dot{\mathbf{w}}$ from equation 2. Therefore: $\mathbf{a}=\dot{\mathbf{w}}$, which is equation (11).

c. *Equation (12) obtained as a restriction of (10).* Take for system XYZ the three principal axes of inertia of the body of reference. For a point ϵ of this body the condition of rigidity gives $\dot{\mathbf{r}}_\epsilon=0$, $\ddot{\mathbf{r}}_\epsilon=0$. In virtue of this, equation (10), applied to all points ϵ, leads to

$$-\Sigma_\epsilon \mathbf{r}_\epsilon \times m_\epsilon(\mathbf{a}\times\mathbf{r}_\epsilon)+\Sigma_\epsilon \mathbf{r}_\epsilon \times m_\epsilon\{\mathbf{w}\times(\mathbf{w}\times\mathbf{r}^\epsilon)\}=\Sigma_\epsilon \mathbf{r}_\epsilon\times\mathbf{F}_\epsilon, \tag{25}$$

which written out for the axes X, Y and Z is equation (12b).

Eq. (10b) can be left out for this proof, as it is a consequence of (10a) and the condition of rigidity, expressed as $\mathbf{r}_\epsilon=$constant. The use of vectors however implies the introduction of the additional coordinates x_1, y_1, z_1, y_2, z_2, z_3, which are all zero (See §5).

d. *Case of plane motion.* In a former publication equations corresponding to (4) of §2 and (10) of §4 have been derived.[5] The origin of the system of axes XY is at point 1, its axis of X passes permanently through point 2. Then Eqs. (10) e.g. reduce to

$$\left.\begin{aligned} x_2(\ddot{x}_\nu-p^2x_\nu)-2p(\dot{x}y_{2\nu}-x_2\dot{y}_\nu)&=x_2\left(\frac{X_\nu}{m_\nu}-\frac{X_1}{m_1}\right)+y_\nu\left(\frac{Y_2}{m_2}-\frac{Y_1}{m_1}\right),\\ x_2(\ddot{y}_\nu-p^2y_\nu)+2p(\dot{x}_2x_\nu-\dot{x}_2x_\nu)&=x_2\left(\frac{Y_\nu}{m_\nu}-\frac{Y_1}{m_1}\right)-x_\nu\left(\frac{Y_2}{m_2}-\frac{Y_1}{m_1}\right),\end{aligned}\right\}\text{(26a)}\Bigg\}\text{(26)}$$

where:

$$p=\frac{\Sigma m\Sigma m(x\dot{y}-y\dot{x})-(\Sigma mx\Sigma m\dot{y}-\Sigma my\Sigma m\dot{x})}{\Sigma m\Sigma m(x^2+y^2)-(\Sigma mx)^2-(\Sigma my)^2}, \tag{26b}$$

which are the analytical equivalent of Newton's equations of motion with Föppl's hypothesis.

9. *Discussion of previous work done on this subject.* Most of the work done on this subject can be considered to consist of two parts:

(1) A negative part, being a criticism of Newton's idea of absolute motion. The main argument is an empirical one, running as follows. The observed motion is relative. Mechanics should deal with observed motions. Therefore mechanics should deal with relative motion in this sense.

(2) An attempt to define the inertial systems, to which motion in Newton's mechanics is referred, in terms of this observed motion, consequently on a relative basis.

[5] Zanstra, Proc. Kon. Acad. van Wet., Amsterdam **23**, 1421, 1921. The same article appeared in the Ann. der Physik (IV) **70**, 153, 1923. As a slight alteration in the formula was made, the reader is referred to the formulas (8) and (9) of the latter article, which are the formulas (4) and (10), derived here, specialized for the plane.

Of the work of some of the main authors we shall give here a very brief review.[6]

Newton's younger contemporary Berkeley[7] criticized Newton's idea of absolute motion. His main argument is the empirical one, that motion in all practical cases of observation is referred to bodies in space. As regards the positive part of his work, he refers to the notion of philosophers who think that ultimately the motion is referred to "the utmost unmoved walls or shell" of "the corporeal world," which in their conception, is finite. This seems to correspond to Copernicus' conception, part of which may be traced back to Aristotle.[8]

In more recent times, since 1870, the interest in these questions was revived by Neumann,[9] who calls attention to the fact that in Newton's mechanics the system of axes to which the motion is referred needs to be specified more clearly. He proposes to refer the motion to a hypothetical body "Alpha." At the same time he wants to retain the idea of absolute motion.

Maxwell,[10] though working out a relative conception for the translation, retains the idea of an absolute rotation, induced to this by experiments like Newton's pail experiment.

Lange and Mach have done much to spread a relative conception of motion. Lange[6] introduced the name "inertial system" and suggested a way of specifying inertial systems experimentally.[11] If we would have trial bodies on which no force was acting, the condition that three of these bodies should move in a straight line would be sufficient to fix inertial systems. In Lange's work much use is made of Newton's "Law of inertia," a principle justly criticised by Mach.

Mach[6] gave an extended criticism of the principles of Newton's mechanics. He reduces the number of fundamental theorems to a minimum and formulates them in a more satisfactory way. For this reference must be made to his original work. We only wish to mention here his interpretation of Newton's pail experiment, where he correlates the alteration in the level of the water with the motion of the pail with respect to the earth and the stars.

[6] For a more complete treatment see: L. Lange, Geschichtliche Entwickelung des Bewegungsbegriffs; E. Mach, Die Mechanik in ihrer Entwickelung; and Enzyklopedie der Math. Wiss. VI 1, p. 30.

[7] G. Berkeley, The Principles of Human Knowledge, Sections 111 et seq.

[8] L. Lange. loc. cit.[6]

[9] C. Neumann, Ueber die Prinzipien der Galilei-Newtonschen Mechanik.

[10] Maxwell, Matter and Motion.

[11] H. Seeliger, Sitz. Math. Phys. Kl. Bayr. Acad. Wiss. **36**, 85, 1906.

Boltzmann's[12] suggestion to refer the motion to the principal axes of inertia of the universe would be of great importance, if this system of reference would lead to the Newtonian equations. A form of the equations of motion in this system of reference, equations which are the analytical equivalent of Newton's equations with Föppl's hypothesis, is given in §7.

Föppl[13] in making his hypothesis that the total angular momentum of the universe vanishes permanently for a principal system of reference (§3), gave a satisfactory solution of the problem of how to specify inertial systems in terms of observed motions (see §6). In §3 it has been assumed that the number of material points in space is finite. It seems, however, that all the results obtained in this article can be maintained for an infinite number of points when in addition to that it is assumed that the rotation of the radius vector $\mathbf{r}_\nu$ of a point ν approaches a definite limit $\mathbf{u}$, when r_ν approaches infinity.

Föppl has pointed out that his hypothesis may lead to an experimental specification of the inertial system to which e.g. the motion of planets should be referred. This of course can only be done when an assumption is made concerning the bodies not yet observed. The inertial system, thus obtained, might be slightly different from the inertial system which is used now, but would presumably come very close to the empirical system.

The positive part of the work of all the authors mentioned above is a definition of inertial systems on a relative basis.

As regards the introduction of relative coordinates and the derivation of invariant equations attention should be called to Kolkmeyer's work.[14] The problems studied by him are more extensive in many respects; he deals e.g. with the elimination of absolute time.

Kolkmeyer works out the relativation of motion without introducing Föppl's hypothesis. For the general insight in the consequences of such a relativation the equations (4) of §2 may serve. As regards the invariant equations we may remark, that such equations can be obtained without introducing Föppl's hypothesis, but again they are of a higher order than equations (22). It does not seem that Kolkmeyer makes a sharp distinction between the introduction of relative coordinates, as distances, and the derivation of invariant equations.

[12] Boltzmann. Vorlesungen über die Prinzipien der Mechanik. Leipzig 1904. C. Neumann[9] made a similar suggestion, which however is quite contradictory to some of his other statements.

[13] A. Föppl, Vorlesungen über technische Mechanik, VI, Erster Abschnitt, Die relative Bewegung.

[14] N. H. Kolkmeyer, Eliminatie van de begrippen assenstelsel, lengte en tijd uit de vergelijkingen voor de planetenbewegingen, Thesis, Amsterdam, 1915.

The review given here shows that the present article is a continuation of a line of thought to which many authors have contributed. This line differs widely from the one followed in Einstein's theories, its primary need being to give a conception which is as close as possible to the way in which observations are actually performed. In the opinion of the author invariant equations do not offer a complete solution of the problem of relativation so as to satisfy the physicist. Such a solution is rather obtained by the introduction of relative coordinates in the equation of motion. This can be done in Newton's theory and there is reason to suppose that it can be done in Einstein's theories also, though the problem seems to be one of no small mathematical difficulty. The purpose of the present article is to show how it can be done in the rather simple case of Newtonian mechanics and for those who are interested in problems of this kind, the next thing is to treat electromagnetic and optical phenomena by a similar method. In our opinion the expression of the motion of particles with respect to other particles is the result of a method of treatment, not the privilege of any special theory. We do not believe that such a method has been applied to Einstein's theories as yet. Let us take e.g. in Einstein's general theory the case where a heavy and a light particle are the only two bodies in space. The theory in its present form gives for the exact solution of this problem,[15] that the measured distance ρ of the particles and a certain angle φ are both certain definite functions of a time coordinate t, if the observer is at rest with respect to the heavy particle, and the question arises as to what the angle φ means, since the only measurable space quantity is the distance ρ. One may be able to evade this difficulty by assuming that the boundary conditions are satisfied if other bodies are present only at a large distance (practically infinity). It seems that instead of this an hypothesis similar to that of Föppl may be used to simplify the problem so as to give a definite answer. We are so bold as to suggest that as a result of such a general hypothesis one will obtain the present solution with the restriction $d\varphi/dt=0$.

For the present article criticisms and suggestions from many persons have been helpful to the author. More especially he is greatly indebted to Dr. A. Korevaar, at present privaat-docent for industrial chemistry in the University of Leiden, and to Professor W. F. G. Swann, to the former for frequent discussions which did a great deal in fixing the fundamental ideas, to the latter for help in the progress of the work at a later stage, and also in the final expression of the results.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MINNESOTA,
August 28, 1923.

[15] K. Schwarzschild, Sitz. Preus. Akad. der Wiss., Berlin 1916, p. 189.

BOOK REVIEWS AND NOTICES

Report on Radiation and the Quantum-Theory. J. H. JEANS. Second edition. This Report gives by far the best account that has appeared of the need for, and development of, a quantum-theory. At the time of the first edition which appeared in 1914, the application of the quantum-theory, by Bohr, to spectral lines had only just begun; and the success which this theory has had, in the intervening years, in the broad field of spectroscopy, has removed the need of making this second edition, as the author says of the first, an *apologia* for the theory.

The crucial test of a quantum-theory is taken to be the experimental fact that the total radiant energy per unit volume in temperature-equilibrium with matter is finite, and not infinite. Classical dynamics is shown to lead necessarily to an infinite density of radiant energy. The development of the quantum-theory began with Planck's assumption that the material energy of vibrating resonators can exist only in complete quanta, and with the aid of this supposition Planck was able to obtain his formula, which has so far satisfied all experimental tests. An account is given of Einstein's method of deriving Planck's formula, making use of the different assumption that it is radiant energy, and not the energy of resonators, that can exist only in complete quanta.

There follow chapters on "The Spectra of the Elements and the Emission of Radiation," "The Photo-Electric Effect and the Absorption of Radiation," and "The Specific Heat of Solids." The chapter on "The Dynamics of the Quantum-Theory" is wholly new since the first Report. In the final chapter on "The Physical Basis for the Quantum-Theory," some of the difficulties of the theory, and possibilities of their solution, are sketched.

The Report is written in the lucid style familiar to the readers of the author's other works, and can be strongly recommended to those who desire to obtain a knowledge of the development and achievements of the quantum-theory.—Pp. 86. The Physical Society of London, 1924. E. P. ADAMS.

La Mécanique Nouvelle. HENRI POINCARÉ.—This volume takes its name from that of a lecture delivered by Poincaré before the Association Française pour l'Avancement des Sciences, at Lille, in 1909. The "New Mechanics" is that of the theory of relativity, and although written before Einstein had developed his general theory, it is still of value for its clear exposition of the necessity for changing our old ideas, as well as for its insistence that the study of the classical mechanics is still of fundamental importance.

The main part of the volume is taken up by a reprint of Poincaré's famous paper, "Sur la Dynamique de l'Electron," first published in 1906 in the Rendiconti del Circolo Matematico di Palermo. It is in that paper that Poincaré introduced, for the first time, the idea of an imaginary fourth dimension, which later led to such important developments by Minkowski. He also introduced, in that paper, the concept of a universal pressure necessary for the equilibrium of an electron, and with the aid of this conception he made an attempt to bring gravitation into the realm of electromagnetic phenomena.

An introduction to this volume, by Édouard Guillaume, gives an appreciation of the part played by Poincaré in the development of the theory of relativity.

The publishers are to be congratulated on making readily available these contributions of Poincaré, which must be regarded as among the really important ones that have led to the development of our modern ideas.—Pp. 81. Gauthier-Villars, Paris, 1924.
E. P. ADAMS.

The Atom and the Bohr Theory of Its Structure. H. A. KRAMERS AND HELGE HOLST, Copenhagen. Translated from the Danish by R. B. Lindsay and Rachel T. Lindsay.—In the foreword, Sir Ernest Rutherford says, "This volume gives a simple and interesting account of our knowledge of atomic structure, with special reference to the work of Professor Bohr. Dr. Kramers is in an especially fortunate position to give a first-hand account of this subject, for he has been a valued assistant to Professor Bohr in developing his theories, and has himself made important original contributions to our knowledge in this branch of inquiry. I can confidently recommend this book to English readers as a clearly written and accurate account of the development of our ideas on atomic structure. It is written in simple language, and the essential ideas are explained without mathematical calculations. This book should prove attractive not only to the general scientific reader, but also to the student who wishes to gain a broad general idea of this subject before entering into the details of the mathematical theory."—Pp. XII+210; 34 figures and 2 plates; price 10/6 net. Gyldendal, London, 1923.

Atomtheorie des festen Zustandes; Dynamik der Kristallgitter. MAX BORN.—This book functions in a double rôle, appearing as one of the sections of the Encyklopädie der Mathematischen Wissenschaften, and also in Blumenthal's series of monographs on the progress of the mathematical sciences. In this second rôle it is described as the second edition of the Dynamik der Kristallgitter, the first edition of which was issued in 1915 with 122 pages. As one of the series of monographs, the book may be purchased separately. Some such arrangement by which the other sections of the Encyklopädie might be separately purchased is greatly to be desired.

The second edition differs from the first by a very considerable simplification and improvement in the mathematical methods of grating analysis, and by a very valuable collection and summary of the great body of recent experimental work in this field, in large part by Born and his pupils. The book will be indispensable to all workers in this subject.

The fundamental thesis and problem remains the same as in the first edition. The thesis is that crystallized solids may be treated as interpenetrating simple lattices of elements acting on each other with central forces, functions only of the distance of separation; the elements of the simple gratings may be smaller than atoms, and in particular may be individual electrons. The problem is to deduce from such a structure the known properties of solids. In working out the theory the conception is essential that the different simple lattices may be displaced as rigid wholes with respect to each other; this involves a distortion of the atoms.

The thesis is supported by finding in detail what deformations of the lattice structure under external forces will account for the phenomena of elasticity, dielectric excitation, piezo-electricity, electro-striction, double refraction, optical rotation, dispersion, specific heats (introducing quantum assumptions), thermal expansion, pyroelectricity, vaporization, melting, and chemical affinity (in certain classes of compounds). This list of properties with many experimental checks is a formidable one and forces the conviction that this picture of the structure of a solid contains a great deal that is essentially true. Without doubt this work is a great advance on any previous theory of the solid state. Nevertheless, one cannot escape the feeling that in some places the treatment has been over-elaborated, for after all, what we are interested in is not whether a certain model may have many properties like those of actual things, but whether the actual things are like the model. It seems pretty evident that if Bohr is correct in supposing that the atoms contain orbits of high eccentricity in rapid precession the actual structure of solids cannot in all respects be adequately represented by interpenetrating lattices of approximately stationary elements.

There are some minor points of the theory which will require further consideration. The question of the stability of such simple structures as NaCl does not yet seem adequately settled, and there are still a number of very doubtful points in connection with Born's calculation of compressibilities, a subject which plays an important part in the whole scheme of experimental checks.—Pp. 260; price \$0.64 in paper, \$0.83 in cloth. B. G. Teubner, Leipsig, Berlin, 1923. P. W. BRIDGMAN.

Lehrbuch der Radioaktivität. G. VON HEVESY AND F. PANETH.—The authors of this textbook are well known contributors to radioactivity especially in the physical chemistry of the radio elements. The subject matter is well arranged and logically divided into 27 chapters which include such modern matters as isotopy not only of radioactive elements, where it was first observed, but also of non-radioactive elements, structure of the atoms and the radiations from them, structure of the atomic nucleus, and chapters on the various subjects ordinarily treated in the discussion of radioactivity.

The treatment of the phenomena is brief in nearly all cases but at the end of each chapter there is a sufficiently large bibliography of original papers bearing on the subject matter of the chapter and these references are quite up to date. The authors may be congratulated in writing a book of so small dimensions and containing so much material. Small as it is, the book is, in the opinion of the reviewer, the best book on radioactivity that has come to us from Germany since the publication of Meyer and Schweidler's Radioaktivität.—Pp. X+213. J. A. Barth, Leipsig, 1923. ALOIS F. KOVARIK.

Waves and Ripples. J. A. FLEMING. Third Issue, Revised.—Between the time when Davy and Faraday were delighting their weekly audiences at the Royal Institution with the newly discovered phenomena of electrolysis and electromagnetism and these days when Thomson, Rutherford, Bragg and Aston, are explaining from the same platform the architecture of the atom, a full century has elapsed; but the whole of this long period has been filled with a series of popular lectures on science which in respect to scholarship, brilliance of illustration, and charm of presentation has probably never been equaled. The volume under review is one of this series. It appeared first in 1902 and is a worthy companion of Thompson's *Light, Visible and Invisible* and of Bragg's *World of Sound*.

The plan of the book is to devote two chapters to each of three types of waves, namely, surface waves in water, compressional waves in air, electric waves in space. The two chapters on sound are perhaps the least novel of the six, differing only slightly from various other general treatments, save in an extended and altogether admirable account of the violin. One misses here, however, any reference to the beautiful work of Sabine, Foley and Webster. The last two chapters, devoted to Hertzian waves, leave little to be desired as a bit of clear exposition. They cover a hundred pages and close with a description of the Fleming valve, but of course make no mention of the grid introduced by De Forest in 1907.

At the present moment, the main interest in these lectures attaches to the discussion of water waves, a confessedly difficult subject and one upon which many lances have been broken, since the time when Newton proved that the speed of water waves must vary as the square roots of their length. Here, in company with Gerstner, Weber brothers, Cauchy, Airy, Tait, Kelvin, and Cornish, Professor Fleming is at his best. Such difficult problems as the physics of group-velocity and wave-velocity, the manner in which sea waves are generated by wind, the distinction between rotational and irrotational motion, the exact nature of oblique and rear ship-waves, the three types of ship resistance, and Scott Russell's solitary wave, all these are presented in a stimulating way, against a background of observation and experience that must arouse the curiosity

of any intelligent reader. Every student of physics should find time to read these first two chapters.—Pp. XII+299. Society for Promoting Christian Knowledge, London.

HENRY CREW.

Collected Scientific Papers of John Aitken, LL.D., F.R.S. Edited for the Royal Society of Edinburgh (with introductory memoir) by C. G. KNOTT.—This volume contains all the more original and important of Dr. John Aitken's contributions to science. With few exceptions they deal with outdoor physics, most of them with the problems of condensation, and while furnishing indubitable premises for the mathematical physicist, are themselves entirely non-mathematical. Dr. Aitken's greatest contribution to science was the experimental proof that the water vapor of the atmosphere condenses into fog or cloud droplets only on "dust" nuclei. By a "dust" particle he meant anything on which water vapor condenses on being slightly cooled below the saturation point.

He occasionally got a light fog in "dust"-free air as a result of rapid and marked cooling, owing, as we now know, to the presence of ions. However, there is no trace of proof that such condensation, requiring as it does at least a fourfold supersaturation, ever occurs naturally. The idea that it does, got into the literature by way of a mere suggestion, but so firmly fixed that all the king's horses and all the king's men may never get it out again.

Dr. Aitken's next most important contribution was to our knowledge of dew. He proved that a large part, often much the greater part, of the dew that covers grass and other objects near the ground, comes from the soil beneath and not from the free air above. Furthermore, that the beads of "dew" that tip the blades of grass are essentially exuded sap and not condensed vapor.

Some of the other subjects discussed in this volume are: Glacier motion; oceanic circulation; centrifugal rigidity; sunset colors; dynamics of storms; thermometer shelters; etc.

Because of the subjects treated, the thoroughness and ingenuity of the investigations, and the adaptiveness of the apparatus used to other studies, this book should be in the library of every physical laboratory.—Pp. XXI+591. Cambridge Press, 1923.

W. J. HUMPHREYS.

Electrical Vibration Instruments, an Elementary Textbook on the Behavior and Tests of Telephone Receivers, Oscillographers, and Vibration Galvanometers. A. E. KENNELLY.—It is the object of this book to present, from an electrical engineering standpoint, the characteristics of telephone receivers and other vibrational instruments as reciprocating electric motors. The central idea is the analogy between mechanical and electrical vibration. Motional and acoustic impedance are treated as analagous to electric impedance. The book concludes with fourteen mathematical appendices, including one on the application of Bessel functions to the elementary theory of plate vibration and one on harmonic Analysis.—Pp. X+450, 214 figures, bibliography and index. Macmillan, 1923.

F. BEDELL.

Physikalisch-chemische Tabellen. LANDOLT-BÖRNSTEIN. Fifth edition, enlarged and revised by WALTER A. ROTH AND KARL SCHEEL.—The founders of this work being now dead, it has been revised and brought down to date by others. Ample space is given to new topics such as crystal structure, excitation and ionization potentials, and photo-electricity.—Pp. XVI+1695 in two vols. $45. Julius Springer 1923.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE NEW YORK MEETING, FEBRUARY 23, 1924

The 125th meeting of the American Physical Society was held in Schermerhorn Hall, Columbia University, New York City, on Saturday, February 23, 1924. The presiding officer was Professor Charles E. Mendenhall, President of the Society. The program was divided into a morning and afternoon session with an attendance of about one hundred and fifty.

At the regular meeting of the Council, held on Saturday afternoon, February 23, 1924, the following elections were made: *Transferred from Membership to Fellowship*, L. A. Hazeltine; *elected to Membership*, Richard L. Doan, John C. Fardon, F. D. Haynes, Kanji Honda, Masaharu Hoshiai, Moses Jacobson, W. S. James, Charles F. Kettering, Masazo Kiuti, Isaac Koga, Tsunetaro Kujirai, Franklin D. Martin, Robert S. Mulliken, Charles R. Pitts, Thomas Spooner, Hazen G. Tyler, John D. Whitney, Hideo Yamashita.

The regular scientific session consisted of twenty-six papers, the abstracts of which are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB, *Secretary*.

ABSTRACTS OF PAPERS

1. The structure of the Kα lines of molybdenum. F. K. RICHTMYER and R. C. SPENCER, Cornell University.—Using a molybdenum water-cooled tube and an ionization chamber spectrometer of high resolving power a search was made for the faint lines in the neighborhood of Kα discovered for the lighter elements by Hjalmar and others and attributed to multiply ionized K shells. No lines were found. But certain characteristics of the Kα lines were noted which seem worthy of report. It can be shown that a strictly monochromatic line originating in a target of uniform energy distribution and reflected from a perfect crystal should give a triangle on the energy-wave-length diagram, the width of the base of which depends on the angular width of the slit system. The lines $K\alpha_1$ and $K\alpha_2$ have shapes approximating triangles. The height of the triangle for $K\alpha_1$ is, as found by previous observers, twice that of $K\alpha_2$, but the base of the triangle for $K\alpha_2$ is 20 percent broader than that for $K\alpha_1$, showing that $K\alpha_2$ is a broader line than $K\alpha_1$. By studying the line width as a function of slit width it is shown that the width

of $K\alpha_1$ is probably not greater than .0003 A. It is important, in studying line structure, to give special attention to the distribution of energy over the focal spot. This distribution is by no means uniform and is likely to lead to incorrect conclusions with regard to the shape of the line. The apparent shapes of $K\alpha$ and $K\beta$ are discussed in this connection.

2. N and O x-rays from tungsten. C. T. CHU, University of Pennsylvania.—The method of Richardson and Bazzoni for the measurement of soft x-rays by photo-electric emission has been extended to a detailed study of tungsten. Quartz apparatus was used. The results establish the $N_{1,2}$, O_5 and $O_{3,4}$ levels at voltages which accord with those selected as most probable by Coster and by Hjalmar.

3. Scattering experiments with molybdenum primary x-rays and secondary radiators of elements with atomic numbers 6 to 17. GEORGE L. CLARK, W. W. STIFLER and WM. DUANE, Harvard University.—Spectrometric experiments described in the current Proceedings of the National Academy of Sciences prove that the x-ray beam from a secondary radiator due to primary tungsten rays contain: (1) scattered rays with wave-lengths identical with those in the primary beam; (2) fluorescent rays characteristic of the elements in the radiator; and (3) tertiary rays produced by the impact of K and L photo-electrons on neighboring atoms. The short wave-length limit of these tertiary rays agrees closely with the theory. Continuing these researches we have used primary rays from a molybdenum target and secondary radiators of low atomic number elements: e.g., graphite, ice, aluminium, rock-salt, and sulfur. These extremely delicate experiments show unmistakably the tertiary rays whose angular and wave-length displacements from the Mo characteristic lines increase with increase in atomic number in accordance with the theory. With rocksalt there is evidence of tertiary radiation due to K electrons from both Na and Cl atoms, removed from those atoms by impact of $Mo\beta$ and $Mo\alpha$ rays. The intensity of the tertiary rays decreases with increasing atomic number. Our results with graphite agree with A. H. Compton's experiments with graphite. The fact that in our experiments the wave-lengths of the tertiary bands increase with the atomic numbers of the other elements suggests that the apparent wave-length shift should be attributed to tertiary radiation.

4. On the change of wave-length in x-ray scattering. A. P. WILLS, Columbia University.—An attempt is made to explain the breadth of the lines in the scattered radiation observed by A. H. Compton and by Bergen Davis and also the results found by the latter indicating a wave-length shift depending on the atomic number of the scattering substance. The theory put forward by Compton is modified by assuming that the scattering, at least in part, is due to electrons in the atom and that the time interim between the absorption of a quantum of energy by such an electron and re-emission is finite though very short; in the interim the action of the nucleus upon the electron produces changes in its energy and momentum which affect the theory through the introduction of a term in the expression for the change in wave-length, which accounts for the results found by Compton and Davis.

5. The character of tertiary rays at different angles from the primary rays. WILLIAM DUANE and GEORGE L. CLARK, Harvard University.—In current numbers of the Proceedings of the National Academy the authors are publishing accounts of experiments that show clearly the existence of tertiary x-rays due to the bombardment of secondary photo-electrons emitted by primary x-rays passing through secondary radiators. Careful measurements by means of an accurate x-ray spectrometer indicate that the tertiary rays occupy a band in the spectrum the short wavelength limit of which agrees accurately with the value predicted by the theory we have proposed.

In the above experiments the tertiary rays came from the secondary radiator at right angles to the primary beam. In the research reported in this paper we have examined the tertiary rays at angles of 45° and 135° as well. The short wave-length limit of the tertiary band is the same in each case, but the breadth of the band and, therefore, its average or effective wave-length decreases as the angle decreases. The intensity of the tertiary rays, also, decreases slightly with the angle. The changes in the band may be ascribed to differences in "filtration" and to an effect similar to the shortening of the effective wave-length of primary general x-radiation as the angle made by it with the cathode rays decreases.

6. The influence of a small ionization chamber of light materials on the rate of ionization of the air within it. HARRY CLARK, The Rockefeller Institute for Medical Research.—A small ionization chamber made of bakelite and ambroid, suitable for measuring therapeutic dosage of x-rays, is described. Comparison with a standard guard-plate chamber shows that, for the same radiation, the rate of ionization of air in the small chamber, multiplied by the factor 1.39, equals the rate of ionization in an equal volume of air surrounded only by air of great extent. As a result of the proper choice of dimensions for the chamber this factor varies with wave-length by not more than 2 per cent over the range corresponding to unfiltered 30kv rays and 95kv rays filtered through 5 mm aluminium. It is indicated that the absence of equilibrium in the emission and absorption of fast-moving electrons between the bakelite and the air accounts for the whole effect in the case of hard rays, and for only part of it in the case of the softest rays, the discrepancy being compensated by absorption of the rays in the bakelite. The ability of the chamber to integrate primary and scattered rays is demonstrated by curves showing the variation of the correction factor with the angle of incidence of the rays.

7. Crystal structure of copper manganese alloys. R. A. PATTERSON, Rensselaer Polytechnic Institute.—When manganese is added to copper up to a concentration of about 30 per cent, a solid solution is formed. Manganese atoms replace copper ones in the face centered cubic lattice of the latter. The side of this cube increases from 3.60 A to 3.70 A. In higher concentrations, manganese atoms are much less effective in stretching the copper lattice. At 50 per cent concentration, faint interference spots due to another lattice appear and become more intense in higher concentrations of manganese. At 90 per cent, the face centered cube has increased to 3.74 A. Above 30 per cent most manganese atoms apparently attach themselves to the new lattice. Measurements of the side of the face centered cube relative to that of copper are given to 0.2 per cent for twelve compositions. Although copper manganese alloys have usually been considered as completely miscible they can no longer be regarded as such, at least in the simplest sense, from about 35 per cent on. The minimum melting point at a concentration of 30 to 35 per cent manganese is in complete accord with Rosenhain's conception that the straining of a given lattice by the substitution of new atoms lowers the melting point. Above this concentration, the new lattice apparently adds stability to the structure of the alloy.

8. The atomic models of the alkali metals. R. B. LINDSAY, Yale University.—On a certain simple assumption, the dimensions of the various types of orbits in the Bohr atomic models of the alkali metals are derived. Assuming for a first approximation roughly quantized Keplerian orbits, the field of force in which a given electron moves is calculated as a function of the distance from the nucleus, using the simplifying assumption that each electron influences the orbits of the other electrons as a continuous spherical distribution of electricity about the nucleus possessing such a magnitude that the total charge between any two spherical surfaces about the nucleus is equal to the

fraction of the charge of the electron corresponding to the fraction of the time which the electron during one revolution spends between these surfaces. From the field thus obtained each group of orbits is computed, using the ordinary quantum relations. The values of the dimensions of the alkali ions so obtained are compared with values computed by Grimm and Landé from crystal structure data, and agreement obtained with Grimm's inequality law. The resulting radii of the lithium, sodium, potassium, rubidium and caesium ions come out to be respectively $.40a_0$, $1.15a_0$, $2.20a_0$, $2.74a_0$, and $3.40a_0$, where $a_0 = .532 \times 10^{-8}$cm. The spectral terms of the sharp series of the arc spectra of the alkali metals are also computed and compared with experimental values.

9. A method for the estimation of the average life of excited mercury atoms. LOUIS A. TURNER, Princeton University.—The experiments of Franck and Cario on the dissociation of hydrogen molecules by mercury atoms excited by the absorption of the $1S\text{-}2p_2$ line show an increased rate of dissociation with increased hydrogen pressure. It is shown by simple kinetic theory that the probability that a mercury atom will collide with a hydrogen molecule while still excited is $\tau/(T+\tau)$ where τ is the average life in the excited state and T is the average time between collisions. Setting the rate of dissociation equal to a constant times this probability and substituting for T in terms of the pressure, one obtains an equation which predicts a linear relation between the reciprocals of the hydrogen pressure and the reciprocals of the rates of dissociation. Points so plotted from the experimental data lie on a straight line. From its constants is obtained a value of 7.4×10^{-22} for $\sigma^2\tau$ where σ is the distance between centers of the colliding atoms. Assuming σ to be 10^{-7} cm, $\tau = 7.4 \times 10^{-5}$ sec. This method gives the life of the atom in the $2p_2$ state. If it is put in a metastable state at the first collision it will eventually cause dissociation so that the first collision is effectively a dissociating collision.

10. Some new measurements of the ionization potentials of multiatomic gases. C. A. MACKAY, Princeton University.—Photo-electric electrons were accelerated by an electrostatic field and ionization was produced by collision. The positive ions were collected on a fine wire electrode which was connected to a Compton electrometer. The rate of charging of the electrometer plotted against the accelerating field gave curves showing a sudden change of slope. The voltage at which this break occurred (corrected by Brandt's method) gave the ionization potential. Radiation effects were suppressed. The results for the gases are as follows: H_2 15.8, N_2 16.3, O_2 12.5, HCl 13.8, HBr 13.2, HI 12.8, H_2O 13.2, NH_3 11.1, Cl_2 13.2, Br_2 12.8, I_2 10.0, NO 9.4, CO_2 14.3, CO 14.1 and 15.6, H_2S 10.4, He 24.5. All these values agree fairly well with previous measurements (where available) except that for O_2. It was investigated further by means of a hot filament in place of the target and the low value was again found. In only one case, carbon monoxide, were two values found. Calculations were attempted based on thermo-chemical data for H_2O and H_2S but no result was as low as that found experimentally. This suggested that ionization at the lowest potential consisted of the expulsion of one electron from the molecule, and was not accompanied by dissociation. This is supported by the results of Smyth and also by recent unpublished work carried on by Duffendack.

11. The low voltage arc in oxygen. L. L. LOCKROW, University of Michigan.—A series of tests was made on the low voltage arc in oxygen between an oxide coated platinum filament and a nickel anode. The first tests made with constant filament temperature and different gas pressures indicated the optimum pressure for maintaining the arc at low voltages. Another series of tests made with this pressure and varying filament temperature showed that the arc could not be held below 16.1 volts. Below this voltage no positive ions are formed in the gas and accordingly this value represents

the critical potential for an ionization process. The probable processes are (1) the ionization of the molecule directly, or (2) the dissociation of the molecule and the simultaneous ionization of one atom. Spectrographic studies both in the visible and ultra-violet regions will be continued to distinguish between the two processes by determining the voltages at which the atomic lines and the oxygen bands disappear. The spectrum at 22 volts shows the negative bands, lines of the triplet system and the one line 4368 A, $1S-3P$, of the singlet system.

12. Oscillations in low voltage arcs. CARL ECKART and K. T. COMPTON, Princeton University.—R. Bär, M. v Laue and E. Meyer (Zeits. f. Phys. **20,** 83, 1923) have found oscillations in the low voltage helium arc. The authors have independently found such oscillations in both helium and mercury, but not in hydrogen or nitrogen arcs. Such oscillations apparently explain the apparent maintenance of arcs at voltages too far below the lowest critical potential to be accounted for by initial velocities of emission of electrons from the hot cathode. The existence of these oscillations has been proven by measurements of the maximum and minimum voltage and by the use of a Braun oscillograph. They are intimately connected with the resistance in the arc circuit. If this is low, no oscillations occur. Inductance and capacitance do not seem to be necessary for their maintenance but affect the wave form. The wave form is very irregular and seems to be determined by the critical potentials of the gas. The maximum voltage is always above the lowest radiating potential and the minimum usually below it. The frequency of the oscillations seems to be determined by the time required for the formation and dissipation of the positive space charge around the filament.

13. Intensity relations in the helium arc in the neighborhood of the ionization point. C. B. BAZZONI and J. T. LAY, University of Pennsylvania.—The helium spectrum has been photographed through neutral tinted wedges at various potentials including those immediately above and below the ionization point. Significant differences are observed in the behavior of the co-planar and crossed orbit lines indicating a greater concentration of co-planar atoms at the lower voltages. A study is made of the presence and effects of oscillations or surges giving instantaneous voltages above the voltmeter readings. These observations have a bearing on the maintenance of "undervoltage" arcs.

14. The band spectrum of silicon nitride, and the isotopes of silicon. ROBERT S. MULLIKEN, Harvard University.—(1) The heads of the band spectrum of SiN were measured and empirically formulated by Jevons. With the help of additional measurements the writer has been able to formulate the null-lines in terms of the quantum theory. The result is, $\nu_0 = 24{,}786 + 268.6\ n' - 4.55n'^2 - 0.15n'^3 - 1338.5n + 12.10n^2$, where n' is the initial and n the final vibrational quantum number; n' has values 0 to 10, and n, 0 to 5. The coefficients of the initial state indicate a relatively remarkably low molecular vibration frequency. (2) By measurements on structure lines, the (preliminary and approximate) general formula is obtained, $\nu = \nu_0 \pm 2m\ (0.70 + 0.0050n') + (0.062 - 0.0050n')m^2$. The values of the coefficients indicate further unusual properties in the initial state. (3) Study of the spectrum of BO (formerly ascribed to BN) has shown (Science, Aug. 31, 1923), in accordance with theory, the presence of two closely related sets of bands, one for each of the isotopes $B^{11}O$ and $B^{10}O$. Aston has found Si to contain a probable isotope 29, and a possible 30, in addition to the dominant 28. The atomic weight, 28.063, indicates a ratio of each of the former, if equally abundant, to the latter of about 2 per cent. On this basis each strong head ($Si^{28}N$) in the SiN spectrum should be accompanied by two very weak ones in a direction and at distances specified by the theory. Actually, the expected relations are verified in the case of 13 of the stronger bands—although the initial state again shows abnormality—and both isotopes 29 and 30 are found to be present, the former being rather the more abundant.

15. The effect of heat treatment upon the cathodo-phosphorescence of fluorite. FRANCES G. WICK and JOSEPHINE M. GLEASON, Vassar College.—Specimens of fluorite heated in a resistance furnace to temperatures up to 600°C show increased intensity and longer period of phosphorescence. Specimens fused and oxidized in an oxy-gas flame show luminescence with color and general character radically changed. In natural fluorite and in specimens heated in a furnace, lengthening the period of cathode ray bombardment and repetition of excitations increase the period of phosphorescence up to a saturation point—the usual effect. In fused and oxidized specimens, the same forms of treatment decrease the period—an effect opposite to that commonly observed. The peculiar behavior of the fused material may be due to abnormally rapid increase in conductivity with rise in temperature under cathode rays. Complete explanation may also involve a difference in the nature of the vibrators producing this luminescence from those producing the ordinary type observed in natural fluorite. Spectra of fused samples consist of line-like bands due to rare earth impurities. Rare earth atoms may possibly take the place of other atoms in the crystal lattice, as suggested by Dr. Mendenhall. Spectra of natural fluorites consist principally of broad, diffuse bands probably due to other impurities which do not form such an intimate part of the crystal structure.

16. The effect of light on the behavior of selenium contact rectifiers. ERNEST MERRITT, Cornell University.—Selenium of unusual purity was melted and spread in the form of a thin film on a plate of aluminum. It was then annealed at a temperature of about 200°C for two hours. Contact was made with the front surface by means of a rod of steel or brass whose radius of curvature at the point of contact was about 0.5 mm. The behavior of such contacts is in general similar to that of a high resistance crystal detector. Voltage-current characteristics taken with direct current showed a wide variation in the resistance of different contacts but were remarkably consistent in type. The resistance is least for a current flowing from the selenium to the contact point, and this is the direction of the rectified current for small alternating e.m.fs. With a specimen annealed at 180°C the rectified current was increased by illumination for all voltages. But with a specimen annealed at 200°C the rectified current was reversed (i.e. it flowed from contact point to the selenium) for any e.m.f. greater than about 1 volt while the effect of light was always such as to correspond to a current from selenium to contact point. Most contacts gave a small current on illumination without any applied e.m.f., the current being opposite in direction to the thermal current developed by heating the contact by conduction through the rod. The rectified current for small applied e.m.f. is also opposite to the thermal current due to heating the contact.

17. Electrical resistance, thermo-electric power and crystal structure of the alkali metals. CHARLES C. BIDWELL, Cornell University.—New data on resistance and thermo-electric power for the five alkali metals over the range $-183°C$ to $+300°C$, together with x-ray diffraction patterns for lithium at several temperatures afford the following information. Thermo-electric power lines are straight at lower temperatures, deviating gradually as the melting-point is approached. Corresponding changes occur in the resistance lines. X-ray analysis shows the fading out of the crystal patterns corresponding to these deviations. This fading begins 100° or more below the melting point. Remarkable increases in thermo-electric power and resistance occur as the melting point is approached. The atomic heat of the free electrons, computed from the thermo-electric data, is 0.24 cal. for sodium and potassium at 100°C, and 0.56 cal. for rubidium and caesium at 100°C. These values are too small to account for the observed excess of the atomic heats over the equipartition value. Temperature coefficients of resistance decrease smoothly with increasing atomic weights. In the liquid state, where crystal structure plays no part, there appears a relation between atomic weight and temperature coefficient of resistance (based on the extrapolated values of resistance at 0°C) of the form $(1/\rho_0)d\rho/dT = k/m^3$.

18. Free energy of ions measured by capillary electrode. PAUL B. TAYLOR, Frankford Arsenal.—Cells were constructed with one electrode (mercury) contained in a capillary and completely polarizable, the other reversible to the anion of the electrolyte. IR drops were reduced to a few tenths of a millivolt or less. It is shown that $T = T_0 + Cf(V - V_0)$, where V denotes potential drop across the cell, V_0 the e.m.f. of reversible electrode, T the surface tension of polarized electrode, T_0 a constant, and C depends only on concentration of the electrolyte. Thus a plot of the T vs. V function (an electrocapillary curve) for concentration c_2 may be considered as derived from the function for concentration c_1 by a linear transformation. The constants of the transformation, ΔV_0 and C_2/C_1, may be determined with considerable accuracy from the descending portions of the curves. ΔV_0 gives the difference in free energy of the anion at the two concentrations. The ratio of the change in free energy of the anion to that of the electrolyte is given by ΔV divided by the e.m.f. of the appropriate concentration cell without transference, and was found to be for KCl and NaCl .50 but for KOH above one-tenth normal .85. Transference e.m.fs. can not be computed without knowing this ratio.

19. Experiments on the sign of the electrical layer furthest away from the surface of a solution in contact with air or a metal. RICHARD D. KLEEMAN and CHARLES R. PITTS, Union College.—A stream of air bubbles was sent along the axis of a vertical glass tube containing a solution of a salt or an acid in water, and the fall of potential along the path of the stream measured by two electrodes connected to a galvanometer. These measurements determined the sign of the electrical layer furthest away from the surface of each bubble, which was peeled off by the motion. On giving a tangential motion to the solution near one of the electrodes, which was of the same material as the base of the salt or else platinum (passing no bubbles), the sign of the electrical layer furthest away from the electrode could similarly be determined. This sign depended in some cases on the nature of the electrode and was often different from that obtained with a free surface. It does not seem to be connected in a simple way with the chemical nature of the salt. Over fifty solutions were examined. On combining some of the results obtained with the results of other experiments (R. D. Kleeman and W. Fredrickson, Phys. Rev. **22,** 134, 1923) it appears that the electrical layers adjacent to the metals Al, Ni, Mg, Zn, and Pt in distilled water are of the nature $-++-$.

20. The electric conductivity of suspensions. HUGO FRICKE and STERNE MORSE, Cleveland Clinic Foundation.—A formula is developed for the electrical conductivity of dilute suspensions of homogeneous spheroids in terms of the conductivities of disperse and continuous phases, of volume concentration of the disperse phase and of ratio of the axes of the spheroids. The theory is directly applicable to the determination of the dielectric constant of disperse systems by the substitution of dielectric constants for conductivities in the formula. The well known formula of Clausius-Mossotti is a special case of our general formula. The formula has been confirmed as to conductivities in the cases (1) of cream, using Babcock's test for determining the concentration of butterfat and (2) of suspensions of red blood cells, the volume concentration being determined centrifugally. The formula holds experimentally up to concentrations of about 30 per cent to an accuracy of about 1 per cent. The formula has been employed to determine the conductivity of suspended cells such as bacteria and white blood corpuscles of known volume concentration. Its practical application in various problems involving the investigation of disperse systems (soil analysis, milk analysis, chemistry of gelatin, volume index of blood, graphite suspensions, etc.) is discussed.

21. On the surface tension of colloidal solutions and the size of some colloidal molecules. P. LECOMTE DU NOÜY, The Rockefeller Institute for Medical Research.—The results of four years of experimentation and 38,000 measurements with the ring method are summarized, and the following points are brought out. (1) The surface tension of all colloidal solutions decreases as a function of the time. (2) This drop increases

with increasing dilutions, reaches a maximum, then decreases. (3) For organic colloids (proteins), a sharply defined minimum value of the surface tension corresponds to the maximum drop. At this concentration, a monomolecular layer is formed. (4) The existence of this layer is confirmed by the slower rate of evaporation of this solution, due to the orientation and tight packing of the molecules. (5) A method has thus been developed to compute the length of such molecules and, when the molecular weight is known, the cross section. The length of the molecule of crystalline egg albumin is 52.8×10^{-8}cm. No other method of measuring surface tension can take the time factor into consideration, although this factor is fundamental and general. Measurements require only 20 sec. with the tensiometer (torsion balance) used, so that the absorption curve can be plotted accurately. The readings are made directly in dynes. The improved instrument is described.

22. The diffusion of helium through several widely different glasses. C. C. VAN VOORHIS, Princeton University.—The rate of passage of helium through several widely different glasses was measured at temperatures between 200 and 500°C. The permeabilities of Pyrex glass to helium at 200, 300, 400 and 500° were found to be respectively 0.188, 0.664, 1.904 and 4.274 mm³ (standard conditions) per cm² per hour through a wall 1 mm thick, with the gas at standard density on one side of the wall and a vacuum on the other side. The permeabilities of 702-P glass for the above temperatures are 0.55, 0.60, 0.62 and 0.68 respectively times the values for Pyrex. The rates through "soft" glasses are much less, in some cases being only a few hundredths of those for Pyrex. A study of the glass compositions in connection with the relative permeabilities of the different glasses tested led to the conclusion that increasing the proportions of the acidic oxides SiO_2 and B_2O_3 increases the permeabilities, and increasing the proportions of the basic oxides Na_2O, K_2O, BaO etc. decreases the permeabilities, the effect being roughly in proportion to the basicity of the oxide. Oxides only slightly acidic or basic, such as PbO and Al_2O_3 seem to have practically no effect on the permeabilities.

23. The characteristic of the thermionic vacuum tube, cylindrical type. CHARLES W. CARTER, American Telephone and Telegraph Company (Introduced by G. A. Campbell).—The characteristic of the cylindrical two-electrode tube, including the knee, is deduced by considering, for each elementary filament length Δx, the intersection of the three-halves power and Richardson's equations, which, neglecting initial velocities, determines the minimum saturation potential V_s of the element. V_s is evidently determined by the distribution of temperature and work function; consequently, given these, the total current at an anode voltage V may be computed as the sum of currents from saturated elements: $\Sigma\Delta I_s = \Sigma C V_s^{3/2}\Delta x$ for $V_s < V$ and the remaining three-halves power current $\Sigma\Delta I_{3/2} = \Sigma C V^{3/2}\Delta x$ for $V_s > V$. *Cylindrical diode*, with heating voltage V_f. Considering cooling at the ends, such that $V_s = k$ for the center of the filament, falling linearly to zero at each end over a fraction a/l of the length l, $I = 2Cl/5V_f\left[V^{5/2}/(1+aV_f/lk)^{3/2} - (V-V_f)^{5/2}/(1-aV_f/lk)^{3/2}\right]$ over the principal range. For zero cooling this yields the five-halves power equation. Neglecting filament voltage, $I = ClV^{3/2}(1-6aV/5lk)$. The heating voltage shifts the characteristic to the right by half that voltage. Cooling tends to straighten the three-halves power curve and to prolong the knee of the curve. *Cylindrical triode.* Rough application is made by the familiar substitution $V = V_p/\mu + V_g + \epsilon$.

24. Methods of varying the sensitiveness of ballistic galvanometers. MORTON MASIUS, Worcester Polytechnic Institute.—The throws of a ballistic galvanometer on closed circuit with and without added resistance do not vary inversely as the total resistances because of the change in damping produced by added resistance. General formulas for the change in throws caused by added resistance have been derived for all cases (moderately damped, critically damped, and overdamped galvanometers) and

have been summarized in a table applicable to all galvanometers and suitable for interpolation. With the aid of this table the throws may be changed at will in any desired proportion. A special discharge key has been designed by means of which the difficulties arising from the change in damping may be avoided and throws may be obtained that are inversely proportional to the circuit resistances.

25. The frequency of a Helmholtz resonator with a hyperboloidal mouth. ARTHUR TABER JONES, Smith College.—For a Helmholtz resonator without a mouth the theory developed by Helmholtz gives a frequency of maximum response which is somewhat greater than that found experimentally. Rayleigh's correction for the thickness of the wall leads to a frequency which checks better with experiment. But the theory as given by either Helmholtz or Rayleigh seems rather inconsistent, for it first assumes that the velocity of the air is everywhere so small that its square may be neglected, and then introduces an assumption which makes the velocity at the edge of the mouth infinite. In the present paper the infinite velocity is avoided by assuming that the wall in the neighborhood of the mouth is a hyperboloid of revolution. Even a very flat hyperboloid reduces greatly the theoretical velocity at the edge of the mouth, and it also gives for the frequency a value appreciably lower than that found from Helmholtz's formula.

26. A resonance tube excited by crystals. W. G. CADY, Wesleyan University.—Plates cut from Rochelle salt crystals are cemented on opposite sides of a flat metal rod at its center. By means of amplifying tubes the rod is set into longitudinal vibration at its fundamental frequency, as described by the author a year ago (Phys. Rev. **21,** 371, 1923). If now the rod carries a round disk at one end, and is so mounted that the disk is at the opening of a glass resonance tube, as in the familiar Kundt's arrangement, then the positions of the nodes in the tube may be determined with great accuracy by means of a movable piston. The apparatus has the advantage of relative compactness, since rods less than a meter in length may be used, and the further advantage of furnishing a sustained note. The intensity of vibration is insufficient to produce a visible effect upon lycopodium powder in the tube.

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